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FEASIBILITY OF USING GASPILS
AND OTHER METHODS OF REMOTELY
MEASURING METHANE IN COAL MINES

PHASE I FINAL REPORT

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ν_0	frequency of incident light (cm^{-1})
ν_i	vibrational frequencies (cm^{-1})
σ	molecular cross section (cm^2)
Ω	solid angle (Sr)
λ_0	incident light wavelength (probe) (cm)
N_r	total number of quanta received
N_o	total number of quanta transmitted
Ω_{rec}	receiver solid angle (Sr)
N	methane density (m^{-3})
V_c	the effective volume of scatterer (m^3)
$T_A(\lambda_0)$	the atmospheric transmittance at laser wavelength
$T_A(\lambda_r)$	the atmospheric transmittance at Raman-shifted wavelength
Ω_r	the divergence of the emitted laser beam (Sr)
R	the distance of detection volume (m)
ϵ	system efficiency
ΔR	resolution length (m)
SNR	signal to noise ratio
η	detector quantum efficiency
PRF	pulse rate frequency (sec^{-1})
τ_m	length of measurement (sec)
S_o	instrument function (m^2)
S_m	measurement function (m^2)
K_a	absorption coefficient ($\text{m}^{-1}\text{atm}^{-1}$)
P_o	transmitted power (W)

P_A	received power at absorption wavelength (W)
P_R	received power unaffected by absorption (W)
β	Mie scattering coefficient (m^{-1})
n_c	methane concentration (atm)
P_m	minimum detectable power (W)
NEP	noise equivalent power ($W\ Hz^{-1/2}$)
Δf	amplifier bandwidth (sec^{-1})
c	speed of light (m/sec)
τ	minimum detection time (sec)
τ_p	pulse length (sec)
τ_d	detector response time (sec)
τ_e	integration time (sec)
f	acoustic frequency (sec^{-1})
V_a	acoustic velocity (m/sec)
Δn	birefringence

1.0 INTRODUCTION

The need to accurately measure methane concentrations in underground coal mines has long been recognized. To date, however, the current technology for methane measurement in underground mines has been restricted to ambient samplers which require the sampler or sampling probe to be immersed within the gas mixture. This practice is often cumbersome, time consuming and in certain cases where accessibility is restricted, it can be hazardous.

With the possible implementation of stricter guidelines for methane concentrations it is becoming increasingly more important to simplify the measurement task as well as improving upon the accuracy and versatility of the sensor. Techniques which offer remote detection capability and which have the ability to make a range resolved measurement present an attractive alternative to the in-situ type samplers. Remote methane detectors will simplify the measurement task thereby increasing the measurement frequency and in addition will allow the user to measure methane concentrations anywhere within the line of sight.

The following report summarizes our investigations into the various techniques available for the remote detection of methane. The report is restricted to those systems which are currently being developed or can be easily modified for methane detection in underground coal mines. Since much of the work within this field is still in the development stages and is being performed under contract to the United States Bureau of Mines, the availability of information was limited. In these cases a detailed evaluation of the specific system was not possible.

In addition to reviewing the available systems, the report weighs the advantages and disadvantages of each system and recommends a system for further study in Phase II of this contract. The recommendation is based upon the system criteria as put forth in the contract as well as MONITEQ's understanding of the current and future direction of the applicable technology.

2.0 PROPERTIES OF METHANE USEFUL FOR REMOTE DETECTION

Methane is a spherical top molecule, which does not have a permanent dipole moment and therefore does not exhibit any infrared rotation spectrum. In addition the methane polarizability ellipsoid is a rotational ellipsoid and has a cubic symmetry and any rotation of the molecule does not change the dipole moment induced by an external field. This prohibits any rotational Raman spectrum.

Methane has a tetrahedral geometry which has four fundamental vibrations; a totally symmetric (A_1), a doubly degenerate (E) and two triply degenerate (F_2). All four are Raman active and their frequency shifts are $\nu_1 = 2914 \text{ cm}^{-1}$, $\nu_2 = 1533.3 \text{ cm}^{-1}$, $\nu_3 = 3018.9 \text{ cm}^{-1}$ and $\nu_4 = 1305.9 \text{ cm}^{-1}$ respectively. The only infrared active vibrations are $\nu_3 = 3.3 \text{ }\mu\text{m}$ and $\nu_4 = 7.7 \text{ }\mu\text{m}$.

In the near infrared region there are many overtone and combination bands. The strongest are the $2\nu_3 = 1.66 \text{ }\mu\text{m}$ overtone and the $2\nu_3 + \nu_2 = 1.33 \text{ }\mu\text{m}$ combination band (2).

Raman scattering, fluorescence emission and absorption are molecular specific. Table 1 gives a comparison of the above scattering and absorption process for methane molecules.

Process	Cross Section ($\text{cm}^2/\text{Sr.mol.}$)
Raman	
- UV + visible	10^{-31}
Resonance fluorescence	
- UV + visible	10^{-14} to 10^{-17}
- infrared	10^{-18} to 10^{-23}
Absorption	
- infrared	10^{-17} to 10^{-21}

Table 1: Comparison of Cross Sections of Different Processes for Methane at S.T.P.

From Table 1 it is evident that Raman scattering has the smallest optical cross section and therefore with respect to this criteria is the least attractive technique because of the resulting relatively weak signals. Although resonance fluorescence has a significantly better cross section at low concentrations, the cross section is reduced at higher concentrations due to quenching. In addition, the quenching process is not fully understood due to its complexity and concentration measurements may not be reliable (Ref. 24).

With respect to this particular criteria, infrared absorption techniques are the most attractive because of the relatively large cross sections involved.

3.0 TECHNIQUES FOR THE REMOTE DETECTION OF METHANE

Based upon the review of the properties of methane useful for remote detection and an extensive search of the literature, it appears that there are only three viable techniques for the remote detection of methane in underground mines. The first technique examined is based upon Raman scattering. The two remaining techniques are both based upon the absorption properties of methane in the near infrared region.

Generally these absorption techniques can be separated into two categories. Those which measure the absorption of methane on and off a peak absorption line (differential absorption) and those which use a spectrally matched gas filter to measure methane absorption across a relatively large bandwidth (gas filter correlation). The three techniques are individually examined in the following section.

3.1 Raman Scattering

3.1.1 Introduction

When molecular vibrations and/or rotations produce changes in the molecular polarizability, the molecule will be Raman active. Such changes result in magnitude variation of the induced dipole moment of the molecule in an electric field. If such a molecule is exposed to an incident light of frequency ν_0 the scattered light will contain not only light at frequency ν_0 but also at frequencies $\nu_0 \pm \nu_i$, where ν_i represents the vibrational and/or rotational frequencies. Scattered light at frequency ν_0 is called Rayleigh scattering and at frequencies $\nu_0 \pm \nu_i$ are called Stokes and Anti-Stokes lines, respectively. Stokes lines are stronger than Anti-Stokes lines (higher population in lower energy states) and will be considered here. A comparison of the relative (to N_2) Raman scattering cross sections for a few gases of interest are shown in Figure 1. For nitrogen excited at 337 nm, the Raman differential cross section (Q branch) is $d\sigma/d\Omega = 3.8 \times 10^{-30} \text{ cm}^2/\text{Sr.mol}$.

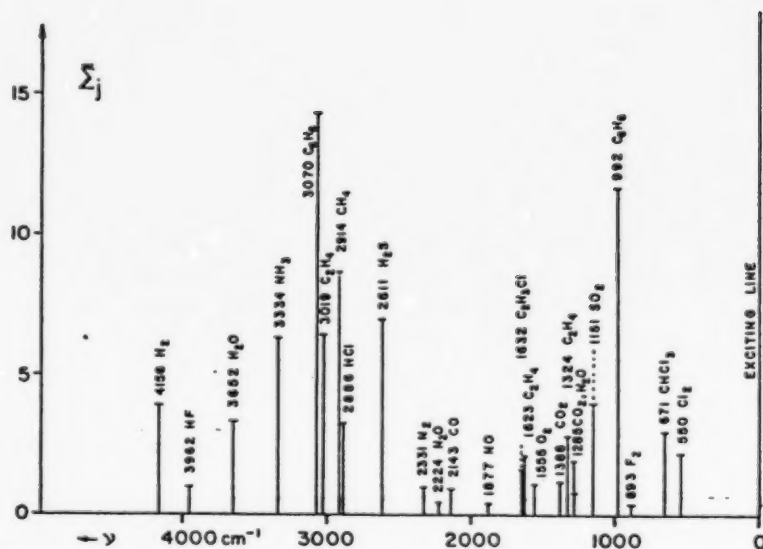


Figure 1: Averaged relative normalized differential Raman scattering cross sections for important gases as function of Raman wavenumber shift. Dotted lines indicate resonance increase in the near UV.

The methane cross section at $\nu_1 = 2914 \text{ cm}^{-1}$, is eight times greater than that of nitrogen and is a good choice for detection of methane. Relative values of methane cross sections at other Raman bands are presented in Table 2 (Ref 4).

Band	Raman Shift cm^{-1}	Relative Values of Cross Section
ν_1	2914	8.0
ν_3	3018.9	4.5
ν_2	1533.3	.24
ν_4	1306	0.008

Table 2: Methane Cross Sections Relative to Q Branch of Nitrogen Fundamental

3.1.2 Choice of the Probing Wavelength

Murray et al (Ref. 5) have shown, the differential cross section follows the relation $d\sigma/d\Omega \propto 1/\lambda_o^4$ where, λ_o = probing wavelength.

The Raman effect produces a weak signal, therefore one tends to choose λ_o as small as possible to achieve a larger signal. Wavelengths in the UV range are more appropriate, however the quantum efficiency of the available detector and the atmospheric transmittance for the chosen wavelength should be considered.

The use of visible wavelengths offers a practical advantage from a systems design standpoint, however at these wavelengths the return signal is smaller due to the reduced differential cross section. More importantly however, is the interference due to coal dust fluorescence. Coal dust fluorescence is present throughout the visible region and because of its relatively large cross section (Table 1) it is not feasible to make visible wavelength Raman measurements in a coal mining environment (Ref. 26).

3.1.3 Signal to Noise Calculation for Backscattered (180°) Raman*

The backscatter (180°) Raman return signal is given by (Ref. 25):

$$N_r = \frac{N_o \epsilon \sigma \Omega_{rec} N V_c T_R(\lambda_o) T_R(\lambda_R)}{\Omega_t R^2} \quad (1)$$

where

N_r : The number of received Raman shifted quanta at the detector

N_o : The total number of quanta emitted at the source

ϵ : Detection system efficiency at the Raman shifted wavelength

Ω_{rec} : Solid angle of receiver (Sr) $= \frac{\pi d^2}{4 R^2}$, where d is the receiver aperture's diameter (m)

R : Detection range (m)

N : Methane density (m^{-3})

V_c : The effective volume from which N are received (m^3)

Ω_r : The divergence of the emitted laser beam (Sr)
 $\Omega_r = A/R^2 = V_c/\Delta R/R^2$, where A and ΔR are the area and length of the effective probed volume

$T_A(\lambda_0)$: Atmospheric transmittance at laser wavelength

$T_A(\lambda_R)$: Atmospheric transmittance at the Raman shifted wavelength

Since the Raman shifted wavelength is close to the incident wavelength the term $T_A(\lambda_0) T_A(\lambda_R)$ can be approximated by $T_A^2(\lambda_0)$. This attenuation term, $T_A^2(\lambda_0)$ arises from the absorption of the atmosphere and the diverse scattering processes such as Mie and Rayleigh scattering (Ref. 25). Also, where the maximum measurement range is less than 30 m and the maximum coal dust concentration is 40 mg/m^3 , $T_A^2(\lambda_0)$ has been shown to be near unity (Ref. 22). Additionally, it has been shown that for short pathlength measurements water vapour does not have a significant effect on the Mie attenuation (Ref. 24). Equation (1) can therefore be reduced to:

$$N_R = \frac{N_0 N \sigma \pi d^2 \epsilon \Delta R}{4 R^2} \quad (2)$$

To attain the desired accuracy in the measurement the ratio of the return to incident signals for shot noise limited detectors (photomultipliers) must satisfy the relationship:

$$\frac{N_R}{N_0} \geq \frac{8 (\text{SNR})^2}{\eta N_0 (\text{PRF}) \tau_m} \quad (3)$$

* For reasons which will become evident later in the report, only 180 backscattered Raman has been considered.

where

SNR : Signal to noise ratio defined by $(\eta N_0)^{1/2} k (\tau_m \text{PRF})^{1/2}$ (Ref. 25)

η : Quantum efficiency of detector

PRF : Pulse rate frequency of laser

τ_m : Measurement time

k : Constant of proportionality; conservatively chosen as $1/2\sqrt{2}$.

Combining equations (2) and (3) results in:

$$\frac{N \sigma \pi d^2 \epsilon \Delta R}{4 R^2} \geq \frac{8 (\text{SNR})^2}{\eta N_0 (\text{PRF}) \tau_m} \quad (4)$$

To make a comparison between the variables which determine the instrument's performance and those which are dependent upon the measurement requirements, the above relationships can be rearranged into measurement and instrument functions (equation 5). The instrument function (S_o) contains all those variables, the values of which are determined by the choice of components. The measurement function (S_m) contains those variables for which the values are determined by the measurement requirements such as, desired SNR, desired measurement accuracy, desired range resolution, etc. By comparing the two functions one can determine if the instrument's performance is capable of meeting or surpassing the requirements imposed by the desired measurement parameters.

$$N_0 \eta (\text{PRF}) \tau_m \epsilon d^2 \geq \frac{32 (\text{SNR})^2 R^2}{N \sigma \pi \Delta R} \quad (5)$$

where $S_o = N_0 \eta (\text{PRF}) \tau_m \epsilon d^2$ (the instrument function) (6)

and $S_m = \frac{32 (\text{SNR})^2 R^2}{N \sigma \pi \Delta R}$ (the measurement function) (7)

where SNR is chosen as the concentration of methane divided by the accuracy of the measurement.

3.1.4 Instrument versus Measurement Function

Assuming the use of commercially available components the instrument function using equation 6, has been calculated to be $S_o = 2.4 \times 10^{17} \text{ cm}^2$. The component characteristics are as follows:

$N_o = 8.5 \times 10^{13}$	photon/pulse	(2.5 mw pulsed nitrogen laser at 337.1 nm)
$\eta = 0.25$		photomultiplier quantum efficiency
PRF = 50	1/sec (Hz)	
$\tau_m = 10$	sec	
$\epsilon = 0.1$		optical system efficiency
$d = 15$	cm	diameter of receiver optics

Figure 2 represents a plot of the measurement function (S_m) for various concentrations of methane at three accuracy levels. Curves a, b, and c represent accuracy levels of 0.1%, 0.15% and 0.2% respectively. The instrument function (S_o) is represented by a horizontal line on the graph. The measurement function was calculated assuming a range of 30 m with a range resolution of 1 m. A listing of the computer program which was used to perform the calculations is given in Appendix I.

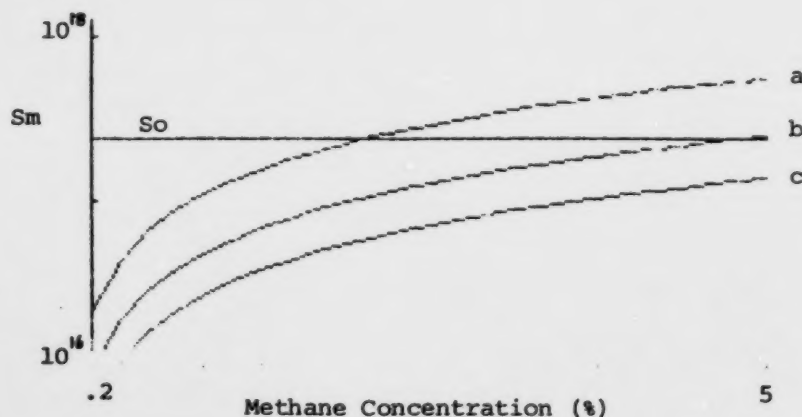


Figure 2: Plot of S_m versus Concentration at 30 m with 1 m Resolution

Figure 2 shows that the instrument function exceeds the requirements of the measurement (the measurement function) for methane concentrations of up to 5% with an accuracy of 0.15%. The figure also shows that such an instrument is capable of measuring methane concentrations up to approximately 2% with an accuracy of 0.1%. Note that for the measurement to be achievable the instrument function must equal or exceed the measurement function.

In summary, the data illustrates that the Raman scattering technique is capable of achieving the desired measurement requirements.

3.2 Differential Absorption Technique

3.2.1 Introduction

Absorption cross sections are the largest among optical interactions. The most sensitive measurement methods use absorption techniques to determine the type and concentration of molecules. Two methods are considered here: single ended long path absorption measurement; where a remote topographical target (Lambertian surface) is used to reflect the energy back toward the receiver and single ended range resolved absorption measurement, where Mie scattering in the atmosphere as a distributed reflector is utilized. Both of these techniques require that the measurement be made within the spectral regions of high atmospheric transparency. In the infrared region, the absorption of H_2O and CO_2 limit the transparency of the atmosphere to between 1.9 - 2.6 μm , 3 - 4.2 μm , 4.4 - 5.4 μm and 8 - 14 μm (Figure 3).

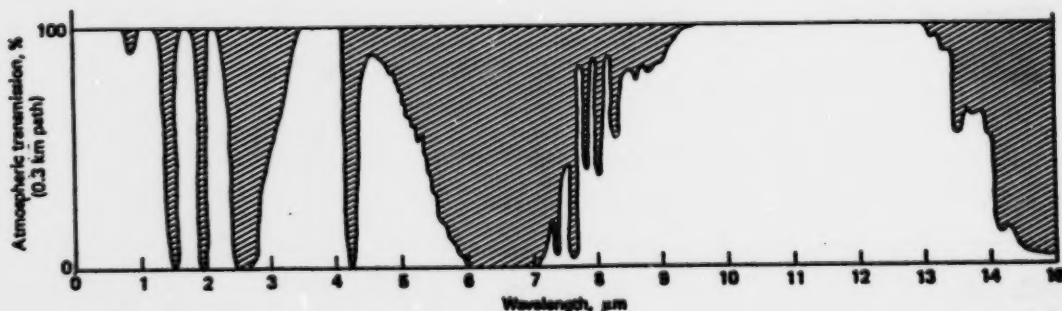


Figure 3: Transmission of the Atmosphere from 0.2 to 15 μm . Hatched areas indicate regions of low atmospheric transmission (Ref. 27).

The strongest absorption lines of methane within the infrared region are given in Table 3.

Vibrational Transitions	$\lambda(\mu\text{m})$
ν_3	3.3
ν_4	7.6
$2\nu_3$	1.66
$\nu_2+2\nu_3$	1.33

Table 3: Absorption of Methane Spectral Lines

Vibrational bands ν_3 and ν_4 are triply degenerate with selection rules $\Delta J = 0, \pm 1$, where J is the rotational quantum number. The infrared spectrum of these bands consists of P, Q, R branches corresponding to $\Delta J = 1, 0, +1$, respectively. The fine structure of the ν_3 spectrum is shown in Figure 4, and those of $2\nu_3$ and $2\nu_3 + \nu_2$ are given in Figures 5 and 6 respectively.

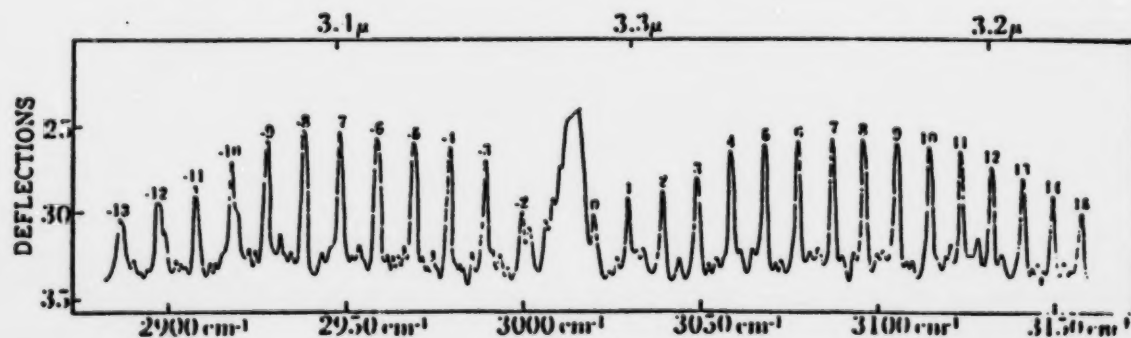


Figure 4: Fine Structure of the Fundamental ν_3 Band of CH_4 at 3.31 μm (atmospheric pressure) (Ref. 1)

Different lines in the spectrum have different absorption cross sections and depending upon the concentration of methane and available laser power, one can tune the laser on and off a particular line. The lines are typically 10 nm apart with a typical width of less than .01 nm. Typical absorption coefficients for methane at different wavelengths are given in Table 4.

Band	Line	$\lambda(\mu\text{m})$	$\alpha(\text{cm}^{-1}\text{atm}^{-1})$	Ref
ν_3	P(7)	3.3913	~8.8	6
$2\nu_3$	Q Branch	1.6654	~.1	7
$2\nu_3 + \nu_2$	Q Branch	1.3312	~.05	7

Table 4: Methane Absorption Coefficients

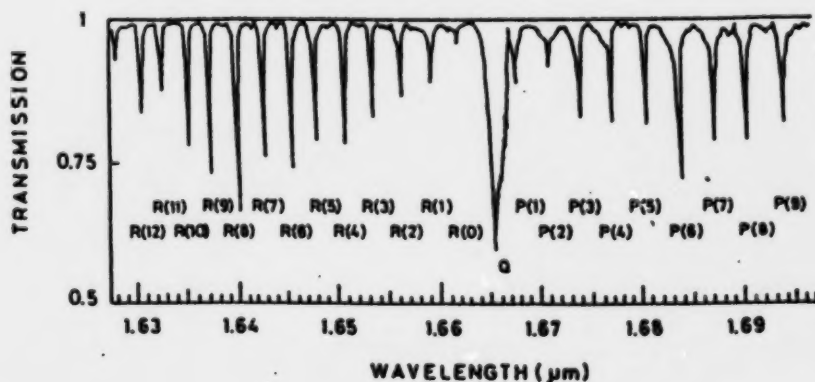


Figure 5: Measured absorption spectra and their assignment of the $2\nu_3$ overtone band of CH_4 molecules in the 1.63 - 1.69 μm region at 60 Torr pressure (Ref. 7)

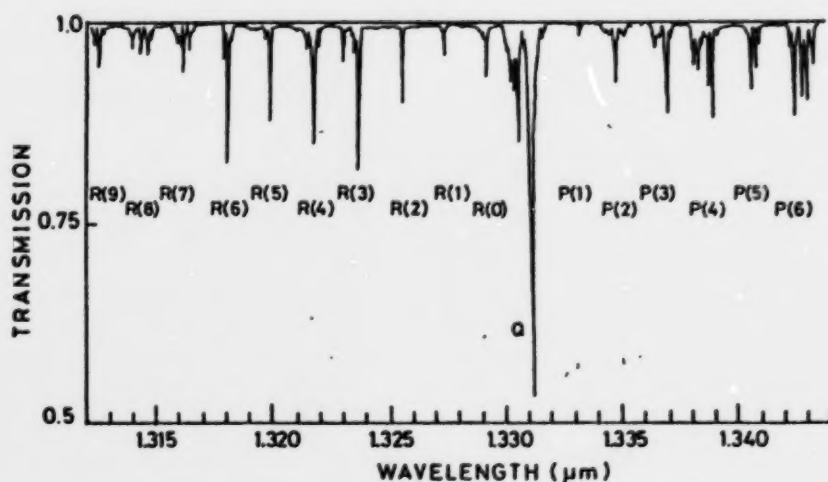


Figure 6: Measured absorption spectra and their assignment of the $\nu_2 + 2\nu_3$ combination band of CH_4 molecules in the 1.31 - 1.35 μm region at 300 Torr pressure (Ref. 21)

3.2.2 Signal to Noise Calculation

Detection of methane relies upon the measurement of both reflected light (P_A) at the absorption wavelength of methane (λ_A) and reflected light (P_R) at a reference wavelength (λ_R) which is not absorbed by methane. Three assumptions are used to generate the following equations, they are:

- The normal methane concentration in the atmosphere is negligible (approximately $2 \times 10^{-4}\%$).
- Attenuation of the signal is largely due to the coal dust.
- The attenuation of the optical system can be varied such that $P_0(\lambda_A) \epsilon(\lambda_A) = P_0(\lambda_R) \epsilon(\lambda_R) = P_0 \epsilon$.

Based upon these assumptions we can write (Ref. 24):

$$P_A = P_0 \epsilon \frac{1}{\pi} \frac{A}{R^2} e^{-2RP} e^{-2K_A} \int_0^R n_c r dr \quad (8)$$

and

$$P_R = P_0 \epsilon \frac{1}{\pi} \frac{A}{R^2} e^{-2RP} \quad (9)$$

where

P_o : is transmitted power W

ϵ : system optical efficiency

f : reflectivity ($= \Delta R \beta/4$ Mie scattering)

A : area of the aperture of receiver $\pi d^2/4$ (m^2)

R : detection range (m)

K_a : absorption coefficient ($m^{-1}atm^{-1}$)

n_c : concentration of methane (atm)

R : methane cloud length (resolution length) (m)

Assuming uniform concentration of methane within the optical path one can write:

$$P_A = P_R e^{-2K_a n_c R} \quad (10)$$

For a dark current limited detector (infrared detectors) the minimum detectable power P_m is given by:

$$P_m \geq \frac{(NEP)(SNR)}{(\gamma_m (PRF)/2)^{1/2}} \quad (11)$$

where NEP is the noise equivalent power of the detector, then P_A ($P_A < P_R$) must satisfy

$$P_A \geq \frac{(NEP)(SNR)}{(\gamma_m (PRF)/2)^{1/2}} \quad (12)$$

combining equation (9) and (10) and comparing with equation 12:

$$\frac{f}{\pi} \frac{A}{R^2} \epsilon P_o e^{-2\beta R} e^{-2n_c K_a R} \geq \frac{(NEP)(SNR)}{(\gamma_m (PRF)/2)^{1/2}} \quad (13)$$

for non-range resolved systems,

and for range resolved systems in an off-axis configuration (see section 4.2)

$$\frac{\Delta R}{4\pi} \frac{\beta}{R^2} \frac{A}{\epsilon} P_o e^{-2\beta R} e^{-2n_c K_a R} \geq \frac{(NEP)(SNR)}{(\gamma_m (PRF/2))^{1/2}} \quad (14)$$

Rearranging the above relations in terms of instrument and measurement functions:

$$(\gamma_m)^{1/2} (PRF/2)^{1/2} d^2 \frac{P_o \epsilon}{NEP} \geq \frac{(SNR) 4R^2 e^{2\beta R} e^{2n_c K_a R}}{f} \quad (15)$$

for non-range resolved systems, and

$$(\gamma_m)^{1/2} (PRF/2)^{1/2} d^2 \frac{P_o \epsilon}{NEP} \geq \frac{(SNR) 16R^2 e^{2\beta R} e^{2n_c K_a R}}{\Delta R \beta} \quad (16)$$

for range resolved systems:

$$\text{where } S_o = (\gamma_m)^{1/2} (PRF/2)^{1/2} d^2 \frac{P_o \epsilon}{NEP} \quad (\text{instrument function}) \quad (17)$$

$$S_{nr} = \frac{(SNR) 4R^2 e^{2\beta R} e^{2n_c K_a R}}{f} \quad (\text{non-range resolved}) \quad (18)$$

$$\text{and } S_{rr} = \frac{(SNR) 16R^2 e^{2\beta R} e^{2n_c K_a R}}{\Delta R \beta} \quad (\text{range resolved}) \quad (19)$$

If the required sensitivity is based on the maximum allowable deviation (Δn_c) from the actual concentration (n_c) then SNR is given by:

$$(SNR) = \frac{1}{1 - \delta} \quad (20)$$

where

$$\delta = e^{-2K_a \Delta n_c \Delta R} \quad (21)$$

Note for differential range resolved measurements the actual SNR will be reduced by a factor of $\sqrt{2}$ due to the signal subtraction.

3.2.3 Instrument versus Measurement Function

Assuming the use of commercially available components, (detailed below) the instrument function has been calculated using equation 17 to be; $S_0 = 2.65 \times 10^7 \text{ m}^2$. The component characteristics are:

$NEP = 6 \times 10^{-10} \text{ W}$ PbS Detector
 $P_o = 0.1 \text{ W}$ Pulsed Flash Lamp
 $PRF = 1000$ Pulses/sec (Hz)
 $\tau_m = 10 \text{ sec}$
 $d = .15 \text{ meters}$
 $\epsilon = 0.1$

Figure 7 is a plot of the measurement function versus methane concentration for a 10 meter total path absorption system (i.e. no spatial resolution). A computer listing of the program to calculate the values is given in Appendix II. The following values have been assumed in the calculation.

$R = 10 \text{ (meters)}$
 $\Delta R = 1 \text{ (meter)}$
 $\beta = 2.8 \times 10^{-3} \text{ m}^{-1}$ (for a dust loading of 25 mg/m^3)
 $K_a = 5 \text{ (m}^{-1} \text{ atm}^{-1})$

Curves a, b, and c, represent accuracies of 0.1%, 0.5% and 1.0% respectively. The figure shows that in an unresolved system, where the source is assumed to be reflected off the coal face, it is possible to measure the methane concentration only up to 3.5% with an accuracy of 0.1%.

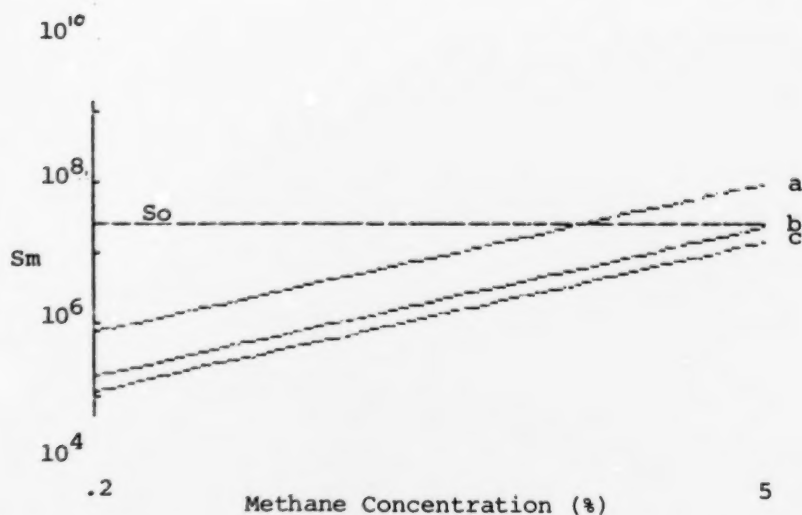


Figure 7: Plot of the Measurement Function versus Concentration for 10 m Total Path Measurements (unresolved measurement)

Figure 8 represents a plot of the methane concentration versus the measurement function for a system capable of range resolution within one meter at a measurement distance of 10 meters. Curves a, b, and c represent accuracy levels of 0.1%, 0.5% and 1% respectively. The plot shows that a methane concentration of 1.5% is achievable, however only with an accuracy of 1.0%. To achieve the desired 5% methane concentration with an accuracy of 0.1% the instrument function will have to be improved by approximately three orders of magnitude.

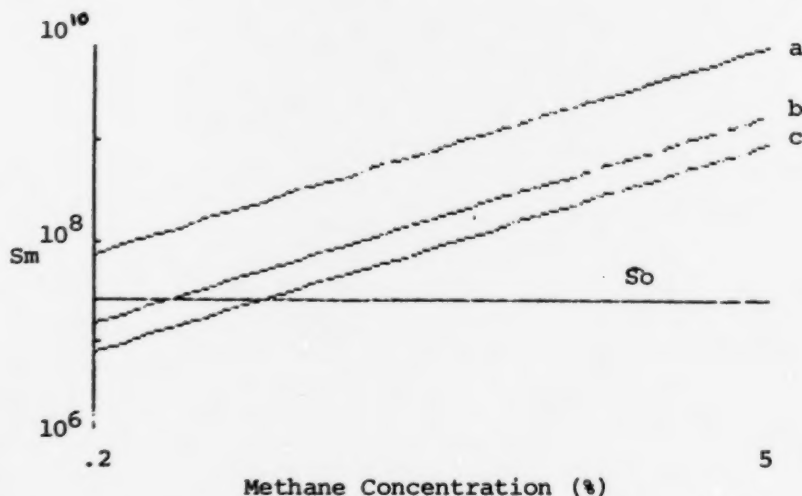


Figure 8: Plot of Measurement Function versus Concentration at 10 m (range resolved system)

Figure 9 represents a plot of the measurement function versus concentration for a range resolved system at a measurement distance of 30 meters. Curves a, b, c, represent accuracy values of 0.1%, 0.5% and 1.0% respectively.

The figure shows that for a distance of 30 meters the instrument function has to be improved by eight orders of magnitude to be able to measure a 5% methane concentration with an accuracy of 0.1%. Note, however that it is possible to achieve methane concentrations of 1.5% with 0.1% accuracy by improving the instrument function only three orders of magnitude. This is possible through the use of cooled Germanium detectors ($NEP = 10^{-14}$ W) and a more powerful (non commercial) laser such as the Er:YAG (10mJ/pulse). This system will be discussed further in the following sections.

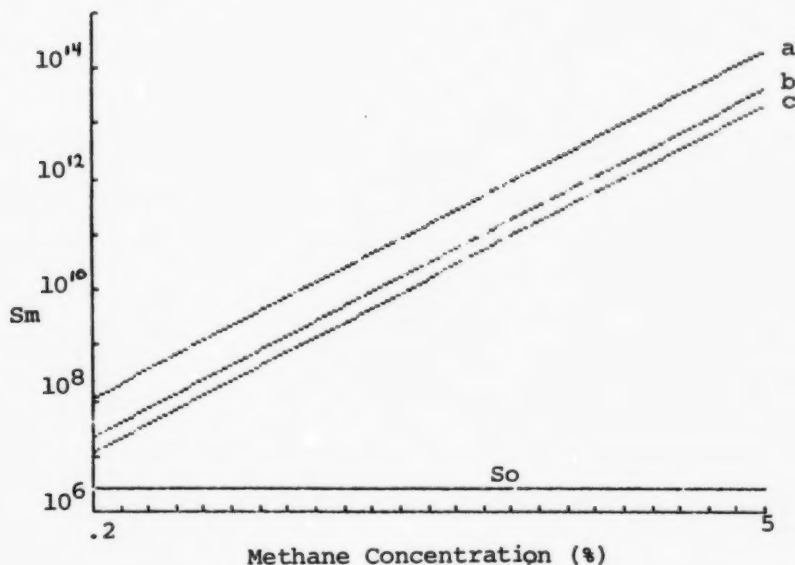


Figure 9: Plot of Measurement Function versus Concentration at 30m for a Range Resolved System

3.3 Gas Filter Correlation

3.3.1 Introduction

The gas filter correlation (GFC) technique is based on the concept that a sample of gas can provide an efficient and selective filter for measuring radiation absorbed by or emitted from a specific target gas. The amount of the specific target gas present is measured by the difference in radiation between passing the incoming radiation through a spectrally neutral filter, and a spectrally matched filter (normally achieved with a sample cell containing the target gas). The GFC technique has high sensitivity because of its large light gathering capability since all wavelengths within a particular region of the spectrum are sampled simultaneously. The technique is also extremely specific since the target gas cell forms a near perfect matched filter with the target gas to be detected and therefore radiation absorbed or emitted by other gases is rejected.

3.3.2 Difference Signal Concept

The basis of operation of the GFC sensor is the differential transmission, of separate reference and measurement gas cells.

$$\text{output} = \text{incoming radiation} \int (\text{cell}_1 - x \cdot \text{cell}_2) d\lambda$$

A gain factor x is chosen to make the sensor cell responses equal when no target gas is present in the sampled atmosphere.

The signal corresponding to the total amount of trace gas in sample volume subtended by the instrument field of view is represented as a difference in energy transmitted between the correlation gas cell and the reference cell. Using a blackbody emitter as the radiation source, one can write the difference signal at the detector as

$$\Delta S = A \Omega \int_{\Delta \nu} (n_c I_o(\nu) e^{-\tau_c(\nu)} - n_r I_o(\nu) e^{-\tau_r(\nu)}) d\nu + J_c \quad (22)$$

where n_c and n_r are the transmission coefficients of the optical components for the correlation channel and reference channel and respectively. $A \Omega$ is the instrument etendue, and $\tau_c(\nu)$ and $\tau_r(\nu)$ are the optical depths of the channels. J_c is the emission term from the correlation gas. $I_o(\nu)$ can be approximated as follows:

$$I_o(\nu) = N_s(\nu) e^{-\tau_s(\nu)} + N_a(\nu) (1 - e^{-\tau_a(\nu)}) \quad (23)$$

where

$N_S(\nu)$ - source radiance at frequency

$N_A(\nu)$ - atmospheric radiance at frequency

$\tau_A(\nu)$ - optical thickness of target gas

Substituting equation (23) into equation (22) one obtains,

$$\Delta S = n_c A \Omega \left\{ \overline{N_S(\nu)} \int_{\Delta \nu} e^{-\tau_A(\nu)} - \frac{n_a}{n_c} e^{-\tau_A(\nu)} d\nu + \right. \\ \left. \overline{N_A(\nu)} \int_{\Delta \nu} (1 - e^{-\tau_A(\nu)}) (e^{-\tau_c(\nu)} - \frac{n_a}{n_c} e^{-\tau_A(\nu)}) d\nu \right\} + J_c \quad (24)$$

where the bar stands for the average over the interval $\Delta \nu$.

Normally the reference channel transmittance is balanced to obtain $\Delta S = J_c$ when there is no methane gas in the atmosphere. Thus,

$$\int_{\Delta \nu} e^{-\tau_A(\nu)} d\nu = \frac{n_a}{n_c} \int_{\Delta \nu} e^{-\tau_A(\nu)} d\nu \quad (25)$$

If we write,

$$T(\nu) = e^{-\tau(\nu)} \quad (26)$$

we get,

$$\frac{n_a}{n_c} = \frac{\overline{T_c}}{\overline{T_A}} \quad (27)$$

and

$$\Delta S = n_c A \Omega (\overline{N_S(\nu)} - \overline{N_A(\nu)}) \int_{\Delta \nu} (T_A T_c - \frac{\overline{T_c}}{\overline{T_A}} T_A T_A) d\nu + J_c \quad (28)$$

Since T_A and T_c are not correlated, further simplification leads to

$$\Delta S = n_c A \Omega (\overline{N_S(\nu)} - \overline{N_A(\nu)}) (\overline{T_A T_c} - \overline{T_A} \cdot \overline{T_c}) \Delta \nu + J_c \quad (29)$$

where $(\overline{T_A T_c} - \overline{T_A} \cdot \overline{T_c})$ is referred to as the "correlation coefficient".

The magnitude of the correlation coefficient determines the ΔS level generated (after balancing) by subsequent signal processing. When no target gas is present in the atmosphere $T_a = 1$ and $T_a T_c = T_c$; thus $\Delta S = J_c$ which is the emission term of the correlation cell and is removed in subsequent signal processing. For any absorbing gas in the atmosphere the ΔS level generated will depend on the concentration and the degree of spectral correlation with gas in the correlation cell. Maximum correlation occurs when the identical gas is in the atmosphere.

3.3.3 Signal to Noise Calculation

Similar to differential absorption techniques, the gas filter correlation (GFC) technique is based upon the infrared absorption spectra of methane. Unlike differential absorption techniques however, the measurement is not restricted to measurements at only two wavelengths. The GFC technique normally encompasses a relatively broad band within the infrared spectrum and involves the fine structure absorption features of a particular target gas, in this case methane.

The signal to noise calculations are therefore extremely complex requiring detailed knowledge of the gas to be sensed. In past, these calculations have been performed with the aid of a modelling program (Ref. 23). One can, however, roughly estimate the performance of the GFC technique using the equations generated for differential absorption techniques (see section 3.2.2). A system performance equivalent to that determined previously (section 3.2.3) is expected.

4.0 SYSTEMS FOR SPATIALLY RESOLVED MEASUREMENTS

For the techniques studied there are basically only two systems used for obtaining spatially resolved measurements. These are systems which utilize a collinear technique and those which use an off-axis technique. Both systems are described and the constraints on each are specified.

4.1 Collinear Systems

A typical arrangement of a collinear system is given in Figure 10. The sampled depth is $\Delta R = c\tau/2$ where c is the speed of light and is determined by the laser pulse length τ_p , the detector response time τ_d , or the electrical integration time τ_e . For a 1 m spatial resolution $\tau = 6$ ns. The location of the 1 m sample is determined by the round trip time of flight of the light pulse.

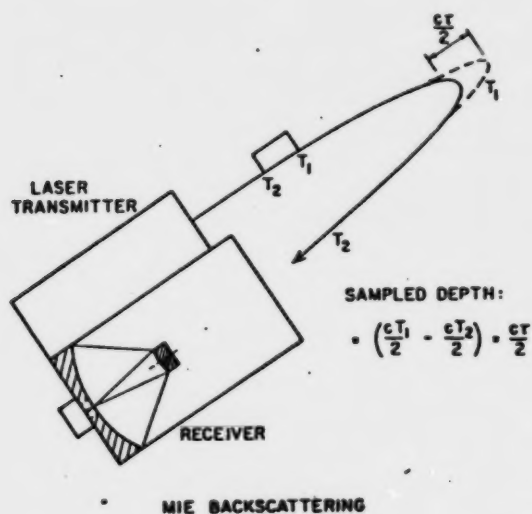


Figure 10: Schematic Diagram of a Depth Resolved Collinear System (Ref. 24)

In this system either the optics are shared between transmitter and receiver or they are arranged coaxially. Shared optics increase the possibility of getting stray light at laser frequency or fluorescence from optics into the receiver detector. A coaxial arrangement requires a larger receiver aperture. A schematic drawing of a typical coaxial system is shown in Figure 11.

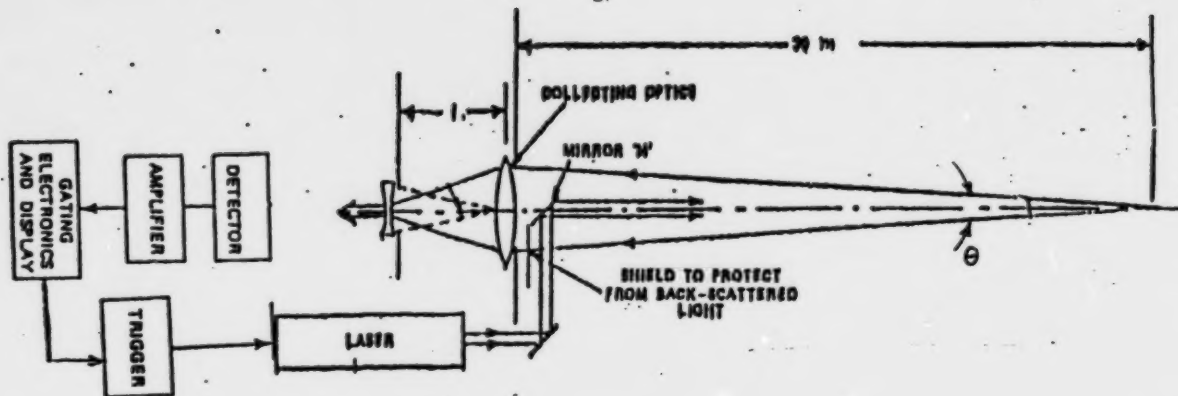


Figure 11: Schematic Diagram of a Collinear/Coaxial System

The laser pulse is transmitted from the central axis of the collecting optics. The 180 degree scattered light is collected by the receiver optics within the angle θ . Assuming the requirement for detection range is from 2 m to 30 m, then for a receiver optics of 15 cm aperture θ varies between 0.075 radians for the shortest distance to 0.005 radians for the farthest distance. The optics therefore should be designed to use aperture masking to allow the total signal to be detected at the 30 m range. At shorter distances the reference signal can be used to correct for loss of intensity.

In a collinear system using a dial technique the collected light is filtered to exclude signals at unwanted wavelengths and two infrared detectors are used to detect the signal on and off the absorption line.

For Raman technique in a collinear system, a grating is used to separate the methane and nitrogen bands and two photomultipliers are used for detection.

Measurements of the detector current are made at discrete intervals through the use of a highly precise, synchronized, variable delay and time gate system. The position in time of "data gates" can be correlated with respect to a reference trigger which enables the electronics to digitize backscatter signal from a scattering volume of any desired distance. The volume of data collected from multiple range gates at laser pulse frequency up to 1000 Hz necessitates a microprocessor to acquire, sort, and preserve the data.

4.2 Off-Axis Configuration (Triangulation)

The schematic drawing of an off-axis system is shown in Figure 12.

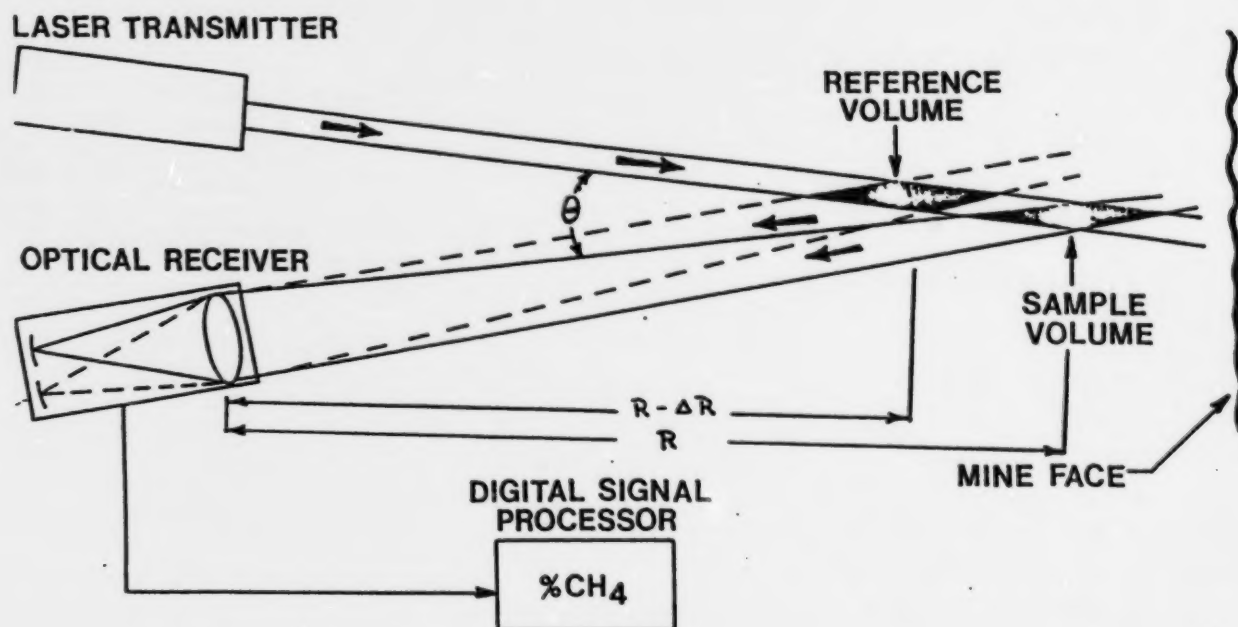


Figure 12: Schematic Diagram of Off-Axis System (Ref. 28)

In this system the field of view of the receiver optics intercepts the transmitted laser light at an angle θ . Nearly backscattered light is detected at ranges R and $R - \Delta R$ by two sets of detectors installed in each set for the methane and reference signals. Either the transmitted laser light or the field of view of the receiver optics is scanned along path R by electronically controlled scanning mirrors. Resolution depth is

adjusted by adjusting the aperture of the receiver optics. For a depth resolution of ΔR and a fixed separation of receiver and transmitter units (d_s) the diameter of the aperture (d) can be approximated at different ranges by (refer to Appendix III for the derivations):

$$\frac{\Delta R}{R} = \frac{d}{d_s + d/2} \quad (30)$$

The constraint on the optics is reduced if the resolution depth is increased at longer distances.

4.3 System Constraints

In a collinear system a resolution depth of 1 m requires the following: a short light source pulse (τ_p less than 2 ns), a fast detector response time (τ_d less than 4 ns) and a short integration time (τ_e less than 4 ns). Also, light source power (P_o), pulse repetition frequency (PRF), detector sensitivity and noise, and the size of the collecting optics (d_c) must satisfy some overall constraints due to the desired measurement time of 10 seconds, and the size and weight limits of a portable system.

For the triangulation system no stringent constraints exist for τ_p , τ_d and τ_e , however, the integration time, and the sensor size and weight require some constraints on P_o , PRF, d_c and detector sensitivity and noise. In this system there are additional constraints on the size of collecting optics because of mechanical range resolving.

5.0 REVIEW OF SYSTEM LIMITING COMPONENTS

The key components in all of the systems studied are the detectors and the radiation sources. The performance of either one or both of these components is usually the limiting factor in determining the overall performance of the sensor package. The following section therefore, reviews the current 'state of the art' of each of these components and where possible, indicates those areas which can be expected to see technological advancement in the near future.

In addition this section includes a review of acousto-optic tunable filters (AOTF) which are being developed to improve upon the versatility of the differential absorption techniques.

5.1 UV Lasers

For the detection of methane using the Raman technique in a collinear system, pulsed UV lasers combined with electronic gating are used. This achieves range resolving and rejects fluorescence background (a slower process compared with Raman) and increased sensitivity of the measurement by signal averaging.

A list of available UV lasers with short pulses are given in Table 5.

Dye lasers are generally too cumbersome to handle, while rare gas excimer lasers are toxic and not completely sealed (Ref. 29 and 31). Solid state lasers are not recommended because of their relatively longer wavelength, which results in lower Raman signal power while frequency quadrupled Nd:YAG (266 nm) lasers which have the shortest pulse length are extremely expensive (\$75K). The Nitrogen laser (337 nm, PRA*, LN103) is the most suitable for this particular application.

All the above lasers are relatively large using voltages high enough to necessitate electrical sealing for use in underground coal mines. Also the UV wavelength at which these lasers operate is harmful to the eye and safety precautions must be undertaken in using such lasers (Ref. 28).

* Photochemical Research Associates Inc.

Type	Laser	λ nm	Peak Power W	PRF Hz	Pulse Length nsec
Dye	Nd-YAG	190	2.3×10^6	30	8
Dye	N2 Excimer or YAG	217	3×10^5	1-300	4-8
Dye	Nd-YAG Second Harmonic	220	$> 10^6$	50	6
Dye	YAG Mode Locked	265	10×10^6	10	.1
Gas	Argon Fluoride Excimer	193		1-200	5
Gas	Nitrogen	337	.23	0-100	.3
Solid State	Nd-YAG	266		10	$.03 \times 10^{-4}$
Solid State	Nd-YAG	355		20	5
Solid State	Ruby	347		1	25

Table 5: Available Pulsed UV Lasers

5.2 Infrared Lasers

Infrared lasers used in dial techniques should be tunable to the structure of one of the following wavelengths $\lambda = 7.6, 3.3, 1.66$ and $1.33 \mu\text{m}$, so that appropriate wavelengths for on and off the absorption line of methane can be selected. A list of infrared lasers useable in the detection of methane is given in Table 6.

Laser	$\lambda(\mu\text{m})$	Energy per Pulse*	Pulse Width*
InGaAsP/InP	1.34	.2 nJ	2 ns
InGaAs/InP	1.65	.2 nJ	2 ns
Er:YAG	1.65	10 mJ	1.5 μs
He-Ne	3.3	.03 W	CW only
D-F	3.4	.7 J	.5 μs

Table 6: Available Infrared Lasers for Methane Detection

Deuterium Fluoride lasers have been used to detect atmospheric methane (Ref. 15), by tuning on the absorption line $3.715252 \mu\text{m}$ (line P1 (Ref. 9)) with an absorption coefficient of $.047 \text{ cm}^{-1} \text{ atm}^{-1}$. The power of the laser is sufficient to permit the experiments to higher concentrations but the size of the laser would limit the apparatus to the laboratory environment. The tunable YAG laser (Nd:YAG pumped LiNbO parametric oscillator/amplifier) has been successfully used to detect methane in the atmosphere (tuning over $1.665\text{--}1.663 \mu\text{m}$) where the interference from water vapour and other hydrocarbons are less than compared with the $3.3 \mu\text{m}$ line. Again, however, the overall size of the system makes it difficult to be taken out of the laboratory.

A portable methane detector has been developed by ERT to detect methane at PPM levels. In this system two HeNe lasers are used as infrared light sources. The first operates at $3.3913 \mu\text{m}$ ($K_a = 8.8 \text{ cm}^{-1} \text{ atm}^{-1}$) and the second operates at $3.3903 \mu\text{m}$ ($K_a = 0.8 \text{ cm}^{-1} \text{ atm}^{-1}$) (Ref. 6 & 17). A topographic target is used to reflect the light from up to 50 feet away for total length absorption measurements with a cooled Germanium detector. Because of the strong absorption of methane at this wavelength, this system would not be suitable for detection of methane at higher concentrations, since the emitted light would be totally absorbed by methane.

* Calculations are approximate since they are based upon manufacturer's reported specifications.

Tunable Diode Lasers (TDL) suffer from low power and difficulty in frequency stabilizing and tuning. Attempts have been made to detect low concentrations of methane in the atmosphere (Ref. 18), using topographic targets or retro reflectors, at the 7.7 μm range. Problems are more severe for TDL at the 1-3 μm range. Currently, the Oregon Graduate Centre is developing an externally grating-tuned cavity diode laser at the 1.65 μm range (Ref. 19). The requirement for laser power becomes more critical at atmospheric pressures. This is because at higher pressures the absorption coefficient increases and also results in broadening of the absorption lines. This broadening, coupled with the broadening due to the Doppler effect upon backscattered radiation makes it more difficult to tune the laser on and off the absorption lines.

In general, pulsed lasers are preferred over CW lasers to achieve better signal averaging. The inability to produce a sufficient number of pulses of equal lengths is another disadvantage of diode lasers.

5.3 Near and Medium Infrared Detectors

5.3.1 Introduction

There are many different types of infrared detectors, but we are interested in those with a high detectivity (defined later) and a fast (1 ns) response time if a collinear range detection system is to be employed.

The regions of infrared radiation we wish to detect are at 1.33, 1.67, and 3.39 μm . Fortunately there are a large number of companies manufacturing infrared detectors, probably spurred by demands from high speed digital fibre optics communications needs and military applications.

The two major classes of infrared devices are semiconductor photocells (quantum detection-charge transport through a solid) and pyroelectrics (thermal detection-materials exhibiting electrical properties which are temperature dependent). Semiconductor devices generally are more sensitive and have faster response times than pyroelectrics. Therefore semiconductor photovoltaic or photoconductive devices are the obvious choice of detectors for high performance requirements. Photoconductive devices have faster response times than photovoltaic detectors but have more detector noise.

5.3.2 Figures of Merit

Although D^* is the most frequently quoted figure of merit in a given application it will be the NEP which will determine the limits of the detector/system response.

Figure 13 shows some detectivities of various infrared detectors versus wavelength. The plot also shows "Ideal Photoconductor, Photovoltaic" responses.

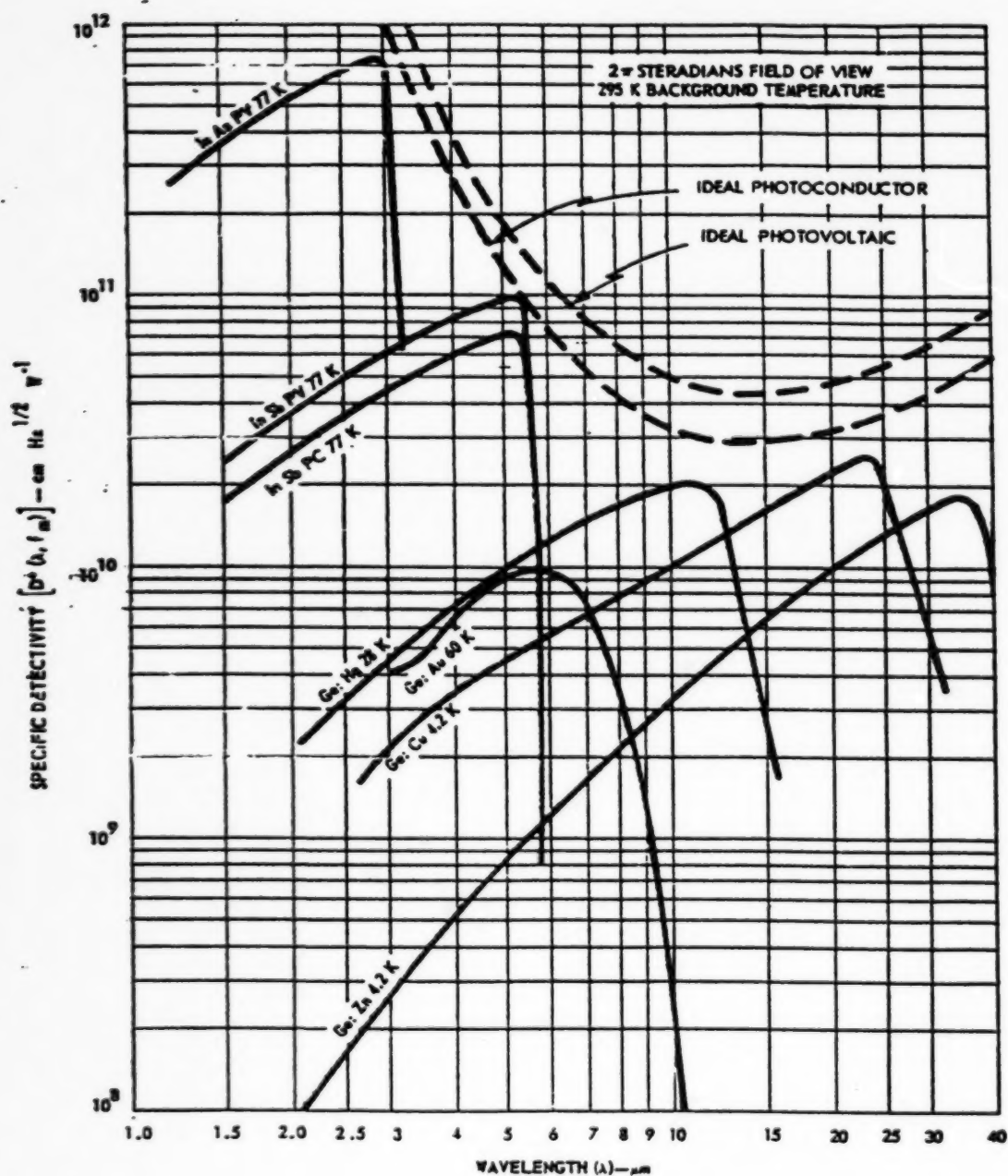


Figure 13: Spectral Detectivities for Above-Average Photo Detectors at Frequency (courtesy Santa Barbara Research Center).

5.3.3 Summary

The final choice of an infrared detector will in large depend upon the wavelength(s) finally chosen to detect methane, the amount of signal available, and the speed of response required, given the bounds of signal available, i.e. weaker signals require detectors with slow responses. Cooled detector operation is advantageous but obviously increases the system complexity. A field of view as narrow as possible should be maintained, to reduce background thermal noise.

It is possible to get detectors in integrated packages containing built-in preamplifiers (Cincinnati Electronics) matched to the detector, but it is not likely that they would be optimized for our requirements. Opto-Electronics has fast (1 ns risetime) near infrared detectors (peak $\lambda = 1.5 \mu\text{m}$) with an NEP of $1 \times 10^{-10} \text{ W} / \sqrt{\text{Hz}}$.

Table 7 shows a summary of some infrared detectors available. It is not likely that infrared detectors will improve much beyond a D^* of 10^{12} . However, there is a thrust from the fibre optics communications area to improve near infrared detector response speed into the picosecond realm while maintaining a high D^* . This, in conjunction with higher powered pulsed semiconductor lasers under development, might allow practical (i.e. small instrument package size) methane detection and ranging in the future.

Detector Type	Peak Response λ	$D^*(\text{cmHz}^{1/2}\text{W}^{-1})$ or $R(\text{AW}^{-1})$	NEP (W Hz^{-1})	Rise Time	Operation Temperature $^{\circ}\text{K}$
PbS Photoconductive	2.2 μm	1×10^{11}	$(3.2 \times 10^{-12})^*$	100-400 μs	298
PbS Photoconductive	2.6 μm	1.6×10^{11}	$(1.1 \times 10^{-12})^*$	300-1100 μs	263
PbS Photoconductive	2.7 μm	3.0×10^{11}	$(1.1 \times 10^{-12})^*$	2-5ms	196
PbSe Photoconductive	3.8 μm	1.0×10^9	$(223 \times 10^{-12})^*$	5-10 μs	298
InAs Photovoltaic	3.1 μm	4.0×10^{11}	$(332 \times 10^{-15})^*$	1 μs	77
Non Avalanche Ge Photovoltaic	1.5 μm	(93×10^6) .25mA/mW	1×10^{-10}	50ps	293
Non Avalanche InGaAsP Photovoltaic	1.65 μm	.4mA/mW		35ps	293
Ge Photovoltaic	1.5 μm	.7A/W 1×10^{12} (77 $^{\circ}$)	1.2×10^{-12}	$\sim 15\text{ns}$	
Ge Photovoltaic	1.4 μm	.8 $\times 10^{11}$ (293) 1×10^{12} (77)	16×10^{-12}	$\sim 10\mu\text{s}$	293-77
Photovoltaic InSb	4.9 μm	up to 20×10^{10}	$(1 \times 10^{-13})^*$	$\sim 50\text{ns}$	77
Photovoltaic Ge	1.5 μm	$\sim .7 \times 10^{10}$	$(\sim 2.5 \times 10^{-11})^*$	$\sim 20\text{ns}$	295
Photovoltaic PbSe	$\sim 4\mu\text{m}$	2×10^{10}		3 μs	
Photovoltaic InSb	$\sim 4.8\mu\text{m}$	$\sim 10^{11}$ (@4.8) (.3-.5 $\times 10^{10}$ 1-3 μm)		1 μs	77
Photovoltaic HgCdTe	$\sim 4\mu\text{m}$	10^8		10-20ns 1ns possible	293
Photovoltaic Ge	1-1.5 μm	.97A/W		15ns or better	
Photovoltaic InSb	1-5 μm	9.4×10^{10}	$.3 \times 10^{-11}$	1 μs	77
Photovoltaic HgCdTe	3-3.5 μm	2×10^8		8ns	
HgCdTe Photoconductive	4.8 μm	10^{11}		2 μs	77
PbSe Photoconductive	1-4.5 μm	1×10^9		1 μs	

* Estimated from Manufacturer's Data

Table 7: Summary of Available Infrared Detectors

5.4 UV Detectors

Because the bandgap energies of silicon and other types of semiconductors are not suitable for UV detection, UV is generally detected using a photoemissive device, i.e. a photomultiplier tube. Various photomultiplier tubes are available to detect radiation from 100 - 400 nm. Quantum efficiencies range from 10 to 20% and response times typically are 1 ns or better (i.e. suitable for range detection). Although quantum efficiencies are low, the gain is high and the noise is low. Gain is a function of applied voltage and the number of dynodes and can vary from as little as 10^3 to as much as 10^8 .

Microchannel plates have a very fast response time (300 ps). However, due to their geometry, quantum efficiency is considerably lower than photomultiplier tubes. Unless ultra-fast response times are required they are best avoided.

Photomultipliers are not necessarily bulky and can be as small as a few inches in length and less than an inch in diameter. High voltage supplies with built-in voltage divider chains can be obtained that plug directly into the base of the photomultiplier tube.

Photomultiplier tubes due to their fast response times, low noise and high amplification are well suited to laser ranging. Laser ranging using a photomultiplier tube would be governed by the Poisson statistics of pulse detection in a quantum noise limited environment. For range detection to 30 m the signal collection time would be 200 ns. If the number of events due to noise per count interval (200 ns) were known and the number per interval with signal plus noise also known the probability of a real signal present would be given by:

$$P(n \geq n_+) = \sum_{r=n_+}^{\infty} \frac{e^{-\bar{n}} (\bar{n})^r}{r!} \quad (31)$$

where n_+ is the threshold count discrimination level and $\bar{n}$ is the average of signal plus noise.

To reduce background counts (noise) to a low level ($\sim 100/\text{sec}$) one can use permanent magnets to allow electrons from only a small central region of the photocathode to reach the first dynode (i.e. small detection area). Also one should choose a photocathode window made of material low in potassium to reduce counts generated by radioactivity.

5.5 Acousto-Optic Tunable Filters (AOTF)

Thallium arsenic selenide ($\text{Ti}_3 \text{As Se}_3$) crystals have been fabricated and operated as AOTF in the near and mid infrared ($1.3 \mu\text{m} - 16 \mu\text{m}$) region (Ref. 20). The advantages of such filters over conventional dispersive systems (gratings or prisms) are increased etendue for a given resolution as well as the possibility for rapid, completely electronic tuning (i.e. mechanical scanning) and programming afforded by acousto-optic interaction.

In an AOTF, phase matching of two optically orthogonal waves is achieved by an acoustic wave (momentum matching of two photons and a phonon). Such a phenomenon can be used to achieve a narrow band optical filter. The peak transmission wavelength can be varied by varying the frequency of the acoustic wave. The tuning relation in a collinear (light and sound propagate in the same direction) AOTF is given by:

$$f = \frac{V_a \Delta n}{\lambda} \quad (32)$$

where

f = Acoustic frequency which is tuned to pass the optical wavelength (Hz)

V_a = Acoustic velocity (3.3×10^4 cm/sec)

Δn = Birefringence (.185)

λ = Optical wavelength (nm)

In a high resolution collinear configuration a high quality crystal is required and to eliminate acoustic standing waves in the crystal one must pulse operate the crystal, such that the acoustic pulse length is made just equal to the time required to fill the crystal.

Attempts have been made (Ref. 10 and 11) to incorporate such filters with a broad band flash lamp to detect methane at $3.31 \mu\text{m}$ range utilizing the dial technique, (required tuning frequency 58 MHz). Such a filter allows for a significant degree of flexibility in the selection of the effective methane absorption coefficient either by changing the effective bandwidth or by selecting the appropriate absorption coefficient. To date, an absorption coefficient of $0.2 \text{ cm}^{-1} \text{ atm}^{-1}$ has been obtained.

6.0 REVIEW OF REPORTED TECHNOLOGIES AND SYSTEMS FOR REMOTE DETECTION OF METHANE

The following section includes a detailed review of the reported technologies for the remote measurement of methane. The first three systems examined are currently being funded or have been funded in whole or in part by the United States Bureau of Mines. For these systems the information was, for the most part, obtained through personal communications.

The remaining systems studied have been developed for methane detection, however not specifically for application in underground coal mines. Where possible system modifications have been suggested to make these systems suitable for underground operation.

A detailed summary of the advantages and disadvantages of each system is included in Section 7.2.

6.1 USBM - (Raman)

To test the possibility of utilizing the Raman technique for detection of methane in underground mines the U.S. Bureau of Mines is developing a prototype Raman Collinear System. A pulsed Nitrogen gas laser (PRA LN100, 337.1 nm) is used with a pulse width of 350 ps with an energy per pulse of 70 μ J. The collecting optics are shielded to cut any unwanted backscattered signal. The Raman signal is weak and adequate filtering of optical noise must be performed.

The noise associated with the signal could fall into two categories (Ref. 9).

- o Out of Band (at laser frequency) due to:
 - Rayleigh scattering
 - Mie scattering (from particulate)
 - Diffuse reflection from coal face
- o In Band Noise (wavelengths the same as methane Raman line) due to:
 - Optics
 - Fluorescence from particulates, the coal face optics and filters

Each of these is considered as follows.

6.1.1 Rayleigh Scattering

The Nitrogen molecule in the atmosphere has a differential cross section two orders of magnitude larger than the methane Raman cross section. Additionally the atmosphere Nitrogen concentration is 78% compared with .2% for methane at the lower limit. The required optical filter must discriminate against laser light by a factor greater than 10^{-5} .

6.1.2 Mie Scattering

Coal dust particulates scatter light at the laser frequency and the differential cross section varies with the type of coal mine. Coal dust concentration varies and could go up to 200 mg/m³. However it has been shown (Ref. 10) that the required rejection is less than 4 orders of magnitude for the worst possible case, and the above filtering for Rayleigh scattering is adequate in this case.

6.1.3 Diffuse Reflections from Coal Face

A coal face with diffuse reflectivity of $\sim .1$ has an effective volume scattering of 10^{10} larger than that of methane in a 1 m pathlength (Ref. 9) and requires the most severe filtering. This has been accomplished with the aid of liquid filters, electronic gating and adjustment of the field of view.

6.1.4 Optics Raman Scattering

Optics material should be chosen such that no Raman scattering due to impurities in the optics coincide with the methane band.

6.1.5 Fluorescence

A fraction of the laser light is absorbed by coal dust and is re-emitted as fluorescence. Fluorescence is broadly distributed in both wavelength and time, and appears in the methane Raman band. However, coal fluorescence (at 390 nm) falls further away from methane band (374 nm) (Ref. 10, 24 and 26), therefore, no filtering is required.

6.1.6 Detection System

A grating is used to resolve the methane and nitrogen (reference) bands and two photomultiplier tubes (anode rise time 2.3 ns with FWHM value of 6.3 ns) are used to detect the signal. Electronic gating (2 ns response time) is applied to achieve .45 m resolution length, but with the limitations on the photomultiplier, two consecutive measurements cannot be achieved.

The system has been able to detect the low concentration levels (0.2%) of methane at a range of 10 m.

6.2 Westinghouse Differential Absorption

Total pathlength methane detection has been successfully demonstrated (Ref. 11) within the range of 10 to 15 m. A broad band Xenon pulsed flash lamp (EG&G, .1 W, 1000 PRF) is collimated by a 12 cm parabolic mirror and the reflected light from the coal surface is detected by a 15 cm receiver at a 45 degree angle from the transmitter (single ended system). The collected light is divided into two paths and is filtered to allow for measurements on and off the absorption line of methane. The first beam is passed through a bandpass filter centered at $3.37 \mu\text{m}$ with a bandwidth of $0.33 \mu\text{m}$. The second beam is passed through a bandpass filter centered at $2.87 \mu\text{m}$ with a bandwidth of $1.47 \mu\text{m}$. Two thermoelectric cooled lead selenide (PbSe) detectors are used for the signal detection.

This system is capable of detection of methane at low concentration (1%) using Mie scattering, however, there is not sufficient power for range resolving.

In a second prototype the Xenon flash lamp was replaced by a more efficient lamp (Krypton) but no information on this has been obtained at this time.

Attempts have been made to develop tunable acousto-optical filters to provide the flexibility of selecting the region of absorption with lower absorption coefficient. The least value achieved has been $.2 (\text{cm}^{-1} \text{ atm}^{-1})$. Further development of the AOTF has ceased due to high expenses involved and lack of support by U.S. Bureau of Mines.

6.3 Homer Research Lab, Bethlehem Steel Corp. (DIAL)

The off-axis differential absorption technique has been used to detect methane concentrations of up to 4% with a depth resolution of 30 cm, at a fixed range of 10 meters. A schematic drawing of the system is shown in Figure 14.

A tunable pulsed Er:YAG laser (Bell lab) at $1.6451 \mu\text{m}$ (1.5 μsec pulse, 10mJ/pulse .25 nm bandwidth, 10 msec time interval) is used to detect methane using the $2\nu_3$ overtone band (Ref. 12).

An intra cavity etalon is used for tuning the laser on and off the absorption peak (.2 nm separation) with a bandwidth of .06 nm. A fraction of the light is passed through a methane cell and is used to adjust for the variation in the etalon tilt angle by monitoring the absorption difference for each pair of pulses on and off the absorption line.

Reflected light from Mie particulates within the two volumes intercepted by the transmitted light beam at distances R and $R-\Delta R$, is collected and detected by two uncooled Germanium detectors which are spatially displaced in the lens focal plane. The detector signal is amplified and processed and the signal is displayed on a digital oscilloscope and concentration is calculated using a computer. The accuracy of measurements at different concentrations as compared with in-situ measurements is shown in Figure 15.

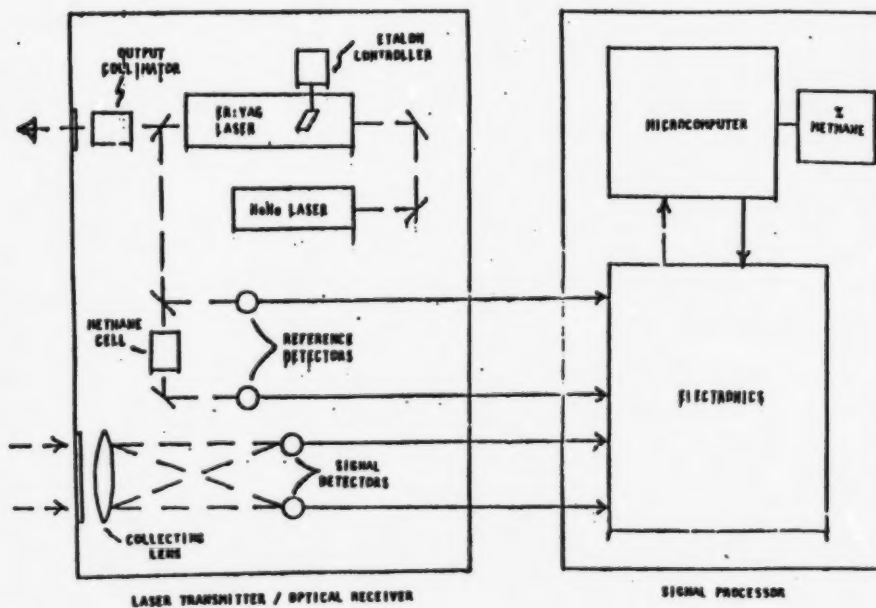


Figure 14: Schematic Drawing of Homer Research Lab Dial System (Ref. 30)

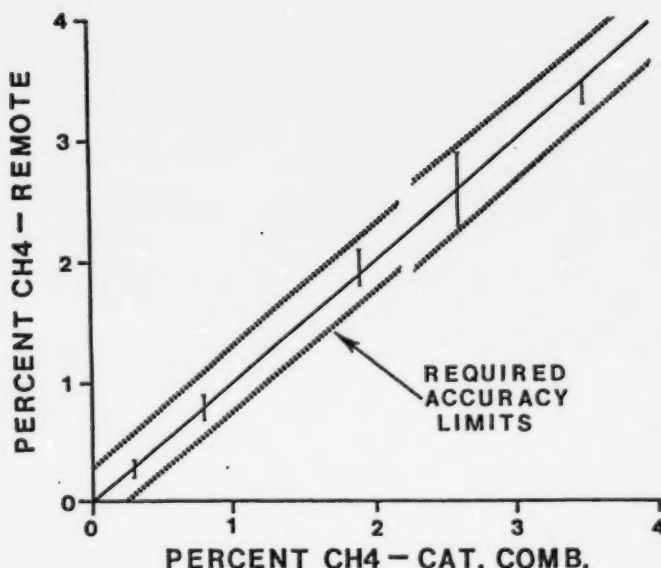


Figure 15: Accuracy of Methane Measurement of Dial as Compared with that of Catalytic Combustion Instrument (Ref. 28)

Including power supplies, the entire system can be fitted into two suitcase size containers. Unfortunately the system is currently capable of making range resolved measurements only at a fixed range. The mechanical modifications required to incorporate a source or optics scanning device would likely increase the package size substantially.

6.4 GASPILS (Gas Pipeline Leak Sensor) MONITEQ Ltd.

The MONITEQ GASPILS sensor was developed as an airborne remote sensor for detecting underground natural gas pipeline leaks. The instrument employs the gas filter correlation (GFC) technique to detect leaks by measuring for the presence of methane above the earth's surface. In its current configuration the instrument uses the earth's blackbody emission as a radiation source and therefore only provides an integrated path measurement. To account for variations in the methane concentration due to sensor altitude the GASPILS is equipped with a second optional channel to measure N_2O . Since N_2O is a common atmospheric gas and not present in pipeline leaks it is possible to eliminate variations due to sensor altitude by ratioing the methane to N_2O . The sensor is shown in Figure 16, and the specifications are detailed in Table 8.

6.4.1 Sensor Description

Upwelling radiation from the earth's surface enters the instrument through an entrance lens, where it is focussed on to the chopper wheel containing the target and reference gas cells.

The chopper wheel consists of an electronics blanking sector, a reference gas sector and a target gas sector. In the GASPILS system there are two target gas sectors, one for N_2O and for CH_4 . The blanking and reference sectors are common to both the N_2O and CH_4 optical trains.

The radiation leaving the chopper wheel is then passed through a second lens, where it is collimated and passed through a passband filter to eliminate stray radiation. The radiation is then focussed on to a liquid nitrogen cooled HgCdTe detector by a third lens.

The signals from the detector(s) are fed first through a pre-amp, a post-amp, a 12 bit A/D convertor and then on to a digital integrator where they are summed to obtain 16 bit accuracy. These values are then input to the system software (Z-80 based) where they are processed through various algorithms to compensate for radiance variations and to calculate the gas and radiance signals. The processed data is then output in both analog and digital formats.

Specifications

Principle of Measurement	Gas Filter Correlation
Data Acquisition Rate	Min: 20 msec Max: 1.28 sec
Detection Limit	20 ppm-M CH ₄ (T=4°C)*
Measurement Range	Detection limit to 1E4 ppm-M CH ₄
Field of View	8 Degrees
Dimensions	
-sensor module	35.5 cm diameter
-electronics module	14 x 45 x 25 cm
Weight	
-sensor module	10 kg
-electronics module	6 kg
Operating Temperature	0 to +40 C
Power Requirements	28 VDC: 200 watts start up : 75 watts nominal operating
Outputs	-RS-232 Multiplexed -7 bit ASCII, 1200 band (selectable) -0 to 10 volt analog -Visual/Audio alarms
Detector Coolant	Liquid Nitrogen, 50 mls per 4 hours

*This nominal value varies from detector to detector as it is dependent on the noise level of the device.

Table 8

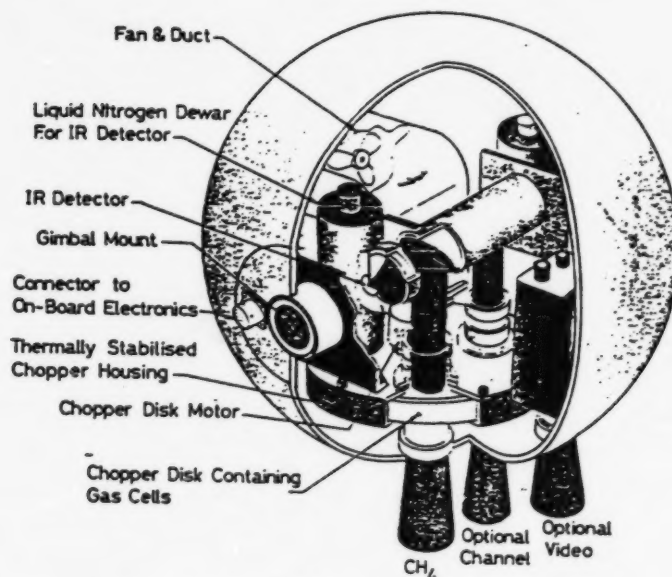


Figure 16: GASPILS Sensor

6.4.2 Sensor Modifications

In its current configuration the GASPILS sensor cannot be considered to be a viable instrument for methane detection in underground coal mines. The primary drawback of the system is that spatial resolution cannot be achieved with a passive system and secondly the wavelength at which it operates ($7.8 \mu\text{m}$) is subject to interference due to the absorption of water (Figure 3). These objections can, however be overcome by modifying the system to include an active source and by adjusting the wavelengths at which it operates.

MONITEQ has developed a prototype OILSPILLS sensor which operates at $3.5 \mu\text{m}$ and uses propane as a target gas to detect oil pipeline leaks. The OILSPILLS sensor is identical to the GASPILS save for the target gas (propane) and the wavelength at which it operates ($3.5 \mu\text{m}$). Since methane also has a strong absorption band centered at $3.3 \mu\text{m}$ it is possible to modify the GASPILS unit to measure methane at this wavelength and thereby avoid the interference due to water absorption.

To achieve the range resolution capability the GASPILS system could be modified to include an active source. MONITEQ is currently utilizing this technique in the development of a Formaldehyde monitor. The Formaldehyde monitor is an ambient monitor which uses an active source and relies on the GFC technique for the detection of trace quantities of Formaldehyde in the atmosphere.

The source chosen for the GASPILS system would have to be a broad band emitter, similar to the Xenon pulsed flash lamp used by Westinghouse. To achieve the spatial resolution requirements it would be necessary to arrange the GASPILS in an off-axis configuration similar to that shown in Figure 12.

6.4.3 System Advantages/Disadvantages

The advantages of the GASPILS system for the measurement are threefold. Firstly, the GASPILS has been developed as a two detector system and can therefore be utilized in its current optical configuration to obtain spatially resolved measurements. Secondly, the signal processing electronics and system operating software have also been developed for a two detector system and can therefore be utilized with only minor modification for achieving spatially resolved measurements. Thirdly, variations of the GASPILS, namely the OILSPILLS and the Formaldehyde monitor, have been developed which utilize an active source and operate at the appropriate wavelength of approximately 3.3 μm .

The two most serious drawbacks of the system however, are the source power requirements and the substantial absorption due to methane at the extreme limits of 5% concentration over a range of 30 m. Initial calculations have shown that a target gas cell absorption equivalent to 300 cm-atm would be required. At such levels it is estimated, that for a range resolved measurements the performance of the GASPILS system would be similar to that of the Westinghouse system. In addition the source power requirements for such a system would likely prohibit the system from being portable.

6.5 Tohoku University-Fibre Optic Differential Absorption

Remote detection of methane has been demonstrated utilizing the dial technique in conjunction with low loss (1 dB/Km) transmission silica optical fibre in the near infrared (Ref. 7 and 21). The experimental set up is shown in Figure 17.

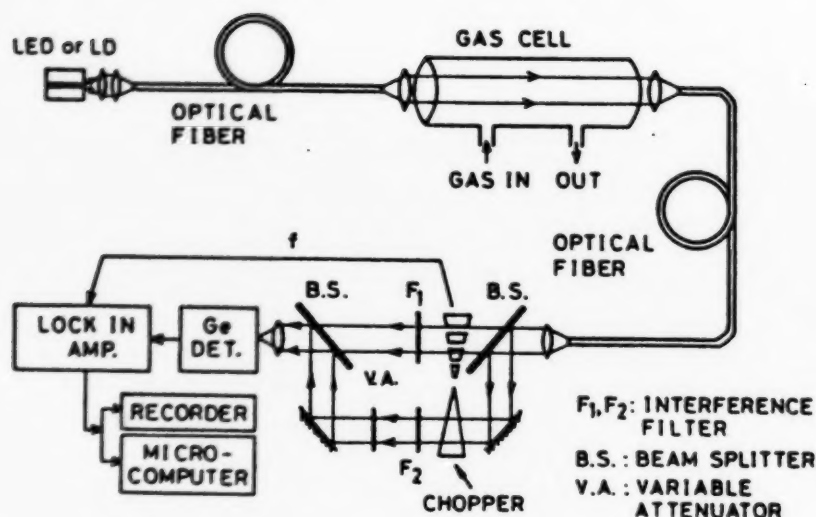


Figure 17: Block Diagram of the Low-Loss Fiber-Optic Wide-Area Remote Sensing System for Differential Absorption Measurements of Various Molecular Species in a Remotely Located Cell Employing Near Infrared InGaAsP Light Source such as a LED or a LD and Dielectric Interference Filters (Ref. 7)

Emitted light from an InGaAsP laser diode (tunable from 0.92 to 1.65 μm) is transmitted by 1 km multimode silica fiber (50 μm diameter core and 125 μm diameter clad) to a cell (50 cm length) with variable methane partial pressure (total pressure of nitrogen and methane was fixed at 1 atm). The same length of fibre was used for the received signal. A beamsplitter divides the beam into two beams. These two beams are chopped (100 Hz frequency) and alternately passed through an on-resonance dielectric interference filter F_1 with transmission centre located at λ_{on} and an off-resonance dielectric interference filter F_2 with transmission centre at λ_{off} . Both beams are detected by a Germanium detector cooled with a dry ice methanol mixture to increase the gain and suppress the noise. A lock-in amplifier synchronizes detection and a micro computer processes the data. To correct for the variations in the power of the diode laser at two different wavelengths (P_{on} and P_{off}), a variable attenuator is used such that:

$$\epsilon(\lambda_{\text{on}}) P_{\text{on}} = \epsilon(\lambda_{\text{off}}) P_{\text{off}} \quad (33)$$

Then one deals only with variation in received power at the two different wavelengths in methane concentration measurements.

At the 1.66 μm range, F_1 is set to 1.666 (on-resonance) with a 3 nm FWHM, and F_2 set to 1.528 μm (off-resonance), with a 5 nm FWHM. A minimum value of 400 ppm (.04%) methane has been detected with this system.

To increase the sensitivity the mechanical chopper can be replaced with a pure stable optical fibre switch. Such a system is promising for air pollution detection at a fixed environment with low concentration levels of methane, and features minimum effect of atmospheric turbulences and ambient lights in a long range detection system.

The use of optical fibres as transmitter and receiver leads to the possibility of using a high power laser which could be kept in the lab along with data processing electronics, and linked to a portable unit containing the optics and scanning unit for range resolving using the fibre.

7.0 EVALUATION OF SYSTEMS FOR METHANE DETECTION WITH RESPECT TO THE SELECTED CRITERIA

To properly evaluate each system with respect to its application for the remote detection of methane in underground coal mines it is first necessary to review the desired system requirements. A review of the system criteria, as put forth in the statement of work, is presented in Section 7.1.

Section 7.2 includes a summary review of each system studied in this report. The advantages and disadvantages of each system are discussed as they pertain to the aforementioned system criteria.

The final section introduces the system which we have proposed for continuation in the second phase of this contract. The advantages and disadvantages of the system are discussed as well as areas which require further development.

7.1 Review of System Selection Criteria

Table 9 has been taken from the original statement of work and defines the desired requirements for a portable, remote, underground methane monitor. Since none of the systems studied were capable of meeting all of the requirements it was necessary to develop a selection criteria in order to evaluate them. Considering the state of the technology and the desired application for the chosen system, the following three criteria were considered to be the most essential.

These are:

- The potential of the system to remotely measure methane concentrations up to 5% with an accuracy of 0.1% within the operating environment.
- The potential of the system to remotely measure such concentrations to a maximum distance of thirty meters with a spatial resolution of one meter or less, within the operating environment.
- The potential of the system to be made portable and be easily integrated into an underground coal mine environment. This includes consideration of the equipment safety, size, weight and power requirements.

The remaining concerns of a system include, the ease of maintenance, measurement time, frequency of measurement, format of outputs and system status indicators. Within reason, all of the above have been given less importance in the evaluation process.

MEASUREMENT

Minimum detectable concentration:	0.2% +/- 0.1%
Maximum detectable concentration:	5.0% +/- 0.1% (preferably to 100% with an accuracy of +/- 0.25% from 5% to 100%)
Location of the methane target:	2 m to 30 m (adaptability to longer distances desirable).
Resolution along the line of sight:	1 m
Dimension across the line of sight:	2 m x 2 m at 30 m
Measurement time:	under 10 seconds
Frequency:	up to 5 measurements in succession during each test and up to 20 test/hour for 10 hours

System must compensate for variation in temperature, moisture, dust, aerosols and other gases.

EQUIPMENT

Power:	battery operated; capable of a minimum 10 hours of continuous use before battery replacement or charging is necessary
Output:	analog; 0-10v DC for chart recorder (optional) digital, 3 digits as follows xx.x
Size:	portable, hand-held
Weight:	5 kg; lighter weight desirable
Indicators:	1 lamp for power; 3 digit LCD for concentration, 1 or more lamps for status.
Maintenance:	all sub-assemblies to be plug-in modules for easy replacement
Standardization & Calibration:	standardization and calibration procedures should be simple and foolproof (fail safe construction)
Malfunction Indicator:	alarms on low battery, out of standardization, faults of basic sub-systems, etc.

OPERATING ENVIRONMENT

Operating temperature:	0 to 40 C
Non-operating temperature:	-20 C to 50 C
Relative humidity:	0 to 100% and aerosols
Dust:	2 to 40 mg/m
Working face conditions:	rock and coal surface is irregular; dry and wet conditions encountered; reflectance of mine face is variable

Table 9: Desired System Specifications

7.2 Review of Reported Systems

The capabilities of each of the systems reviewed in this report are summarized in Table 10. In general, none of the systems examined are currently capable of achieving all three of the desired specifications. A critical review of each system with respect to its potential to meet the three major specifications follows.

7.2.1 USBM: Raman Scattering

The Raman system, which uses the collinear technique for spatial resolution is currently the best of the available systems studied, for methane detection. The unit is capable of spatially resolving (within one meter) methane concentrations up to 5% with an accuracy of 0.3% at the maximum distance of 30 meters. Unfortunately the technique does have some major disadvantages with respect to its operation in an underground environment as well as its portability. In summary these are:

- The laser source emits UV radiation at levels which are at the recommended eye safe level. To meet the desired measurement specifications the laser output would have to be increased beyond the recommended eye safe level and caution would therefore be required by underground staff during operation.
- Both the laser source and the photomultiplier tube utilize high voltage sources which are undesirable in the mine environment.
- The system currently under evaluation by the USBM is restricted to a laboratory environment because of its size and weight. In order to reduce the system to a portable format, major advances in reducing the size of the laser source and detectors will be required. Unfortunately, there is little indication that the technology is being directed towards miniaturization of either, and it is therefore unlikely that a portable system will be developed in the foreseeable future.

In summary, although the Raman system is capable of meeting the range and concentration specifications, it does not meet neither the portability nor the underground integration requirement. In addition, the future growth of the technology is not directed towards miniaturization of UV lasers and it is unlikely that a portable system will be developed in the near future.

7.2.2 Westinghouse: Differential Absorption-Flash Lamp

The system developed by Westinghouse uses a broad band flash lamp as a source which is reflected off the coal face to make an unresolved methane concentration measurement. In its current configuration the system is capable of measuring up to 5% methane with an accuracy of 0.5% over a total pathlength of 10 meters. Although the technique could be used in an off-axis configuration to make spatially resolved measurements, the source power would be inadequate to meet the range and concentration requirements. The main disadvantages of the system with respect to the three major criteria are therefore:

- The power of the sensor flash lamp is insufficient to make range resolved measurements at the desired range and concentration levels.
- Details of the flash lamp have not been made available (it has been specifically modified for this application) however, it is unlikely that its power output can easily be increased to a suitable level while maintaining portability.
- The current system is portable however, implementation of an off-axis configuration would require a major redesign and likely result in, at best, a semi-portable system.

In summary, the Westinghouse system is limited to total pathlength measurements because of insufficient source power. Since details of the flash lamp are not available, we can only speculate as to whether or not the power output can be increased sufficiently. At this time, however, it does not appear that Westinghouse is moving in this direction.

7.2.3 Homer Research Labs: Differential Absorption-Laser

The aforementioned system provides spatially resolved measurements using an off-axis configuration with a pulsed Er:YAG laser as a source. The system is capable of measuring up to 4% methane (stated accuracy of 0.3%) at a maximum distance of 10 meters with a 0.3 meter resolution. Unfortunately the system is currently only capable of a fixed range measurement. It should be possible however to implement a source or detector scanning arrangement to obtain variable range measurements. The major disadvantages of the system are:

- The laser power is insufficient to make the measurement beyond the 10 meter range.

- The system is currently capable of only a fixed range resolved measurement.
- Incorporation of a scanning mechanism to achieve variable ranging will result in an increased instrument size.

In summary, the Homer Research system is capable of making range resolved measurements at or near the desired range and concentration levels. Increased source power and addition of a scanning arrangement should allow the system to meet the desired specifications while still remaining semi-portable. In addition, the infrared laser technology is currently undergoing rapid development and the potential for smaller and more powerful infrared laser sources is promising.

7.2.4 MONITEQ Ltd: GASPILS-Gas Filter Correlation

The modified GASPILS system, described earlier in this report, has two major drawbacks for operation in underground coal mines. These are:

- The absorption required by the gas filter cell (300 atm cm) would be difficult to achieve in a portable system.
- Similar to the Westinghouse system, the power requirements of a broad band source would prohibit a portable battery operated system.

The advantages of the GASPILS system are that it has been developed as a two detector system and could be easily modified to incorporate a differential absorption technique.

7.2.5 Tohoku University - Differential Absorption-Fibre Optic

The aforementioned system is not a true remote sensing technique and in its present configuration is not suitable for our application. The system does however illustrate the use of diode lasers to make a differential absorption measurement through the use of spectral filters.

SYSTEM:	USBM	Westinghouse	Homer Research Lab
Technique:			
- Measurement	Raman Scattering	Differential Absorption	Differential Absorption
- Spatial Resolution	Collinear	N/A	Off-Axis
Methane Detection:			
- Maximum Conc.	5%	5%	4%
- Accuracy	+/- 0.3%	+/- 0.5%	+/- 0.3%
- Range	30 m	10 m	10 m
- Resolution	1 m	N/A	0.3 m
System Specifications:			
- Source	Pulsed N ₂ Laser	Xenon Pulsed Flash Lamp	Er-YAG Pulsed Laser
- Detector(s)	Photomultiplier Tube	TE Cooler PbSe	Uncooled Germanium
- Size	Not Portable	Portable	Semi-Portable
Comments:	Laser Power Exceeds Safety Requirements	No Spatial Resolution	Fixed Spatial Resolution

Table 10: Summary of Reported Technologies

7.3 Selection of Ranging and Measurement Techniques

7.3.1 Ranging Technique

Of the two ranging techniques available the collinear arrangement offers the most advantages. They are:

- Because the emitter and receiver optics are shared the collinear configuration will result in a smaller more portable package compared to an off-axis configuration.
- Although electronically more complex, the collinear arrangement is mechanically much simpler and should therefore result in a more reliable instrument when used in an underground environment.

The only major disadvantage of the collinear system for this application, is that it requires the use of narrow pulse width lasers. This limits the usefulness of the technique, since, as will be discussed, many of the available infrared lasers are not capable of producing sufficiently narrow pulse widths.

7.3.2 Measurement Technique

Of the three techniques available, only Raman scattering and differential absorption offer promise for use in this application. The GFC technique is not a feasible alternative because of the constraints imposed by the relatively high methane concentrations involved.

The advantages of the Raman scattering technique with respect to this application are as follows:

- Each compound has its own unique spectral shift of Raman scattered light. Interference due to other gases is therefore not a problem.
- The intensity of a Raman line is directly proportional to the methane concentration and independent of other gases or coal dust.
- The instantaneous response of the Raman scattering process coupled with available narrow pulse width lasers and fast response detectors allows a collinear arrangement to be utilized.
- Any laser of essentially arbitrary wavelength and bandwidth is capable of being used as a source.
- The technique has been experimentally shown to be capable of nearly achieving the desired measurement specifications.

The disadvantages of the Raman technique are as follows:

- Due to the visible fluorescence of coal dust the Raman scattering technique is limited to operation within the UV region of the spectrum.
- The intensity of UV light emitted from the laser is currently at the recommended eye safe level. To achieve the desired measurement specifications the laser output would have to be increased beyond the recommended eye safe levels.
- The size of currently available lasers prohibit the system from being portable. In addition there does not appear to be a major technological thrust towards miniaturization of UV lasers.
- UV lasers and the photomultipliers used to detect the Raman signal require high voltage sources. These components will therefore require complex shielding for operation in underground coal mines.

In summary, from a technical standpoint the Raman technique is attractive since it has been proven to be nearly capable of achieving the desired measurement specifications. From an operational point of view however, the technique relies on the use of large lasers operating in the UV region and requiring high voltage sources. Additionally, the general thrust of the technology suggests that development of a portable system based upon this technique is unlikely in the near future.

The advantages of the second alternative, differential absorption are as follows:

- The differential absorption technique offers the largest optical cross section which makes this technique the most sensitive for the detection of methane.
- Available detectors do not require high voltages for operation and therefore are more easily engineered for use in a coal mine.
- With respect to eye damage, the infrared radiation necessary for the measurement is substantially safer than the radiation required at UV wavelengths.
- Because of their size, infrared diode lasers offer the promise of a truly portable system. In addition there is a major technological thrust from the military and communication fields towards development of more powerful and more stable diode lasers.

- Available diode lasers are capable of achieving the narrow pulse widths required for use in a collinear arrangement.
- Using an Er:YAG laser as a source the technique has been proven to be nearly capable of achieving the desired measurement specifications.

The disadvantages of the differential absorption technique are:

- The power output of available diode lasers is approximately ten orders of magnitude less than required to achieve the desired measurement specifications. Although there is a major thrust towards improving the output power it is unlikely that it will be improved by greater than two orders of magnitude over the next five years (Ref. 32).
- Alternative infrared lasers (non diode) are not capable of producing the narrow pulse widths required for a collinear arrangement. Ranging techniques are therefore limited to the more cumbersome off-axis configuration.
- Because of their size, non diode infrared lasers prohibit the system from being portable. Similar to UV lasers, there does not appear to be a major technological thrust towards reducing the size of such lasers.

In summary, although the use of non diode infrared lasers to nearly achieve the measurement specifications has been proven, their large size prohibits the development of a portable system. Infrared diode lasers however are small and offer the potential of a portable system. Unfortunately the power output of such lasers is ten orders of magnitude less than that required.

7.4 System Selection

There are two viable alternatives which could be pursued for detailed conceptual design. Both methods utilize infrared differential absorption as the measuring technique. Unfortunately, neither system will be capable of meeting all three of the desired system specifications. A brief summary of each is included.

7.4.1 Semiconductor Laser

A system utilizing an infrared semiconductor laser as the source is an attractive choice because the small size of the laser offers the promise for a truly portable system. In addition semiconductor lasers can be used in a collinear arrangement, thereby simplifying the mechanical design of the instrument. The differential absorption technique would be used to make the measurement through the use of on-resonance and off-resonance filters as previously described (Section 6.5).

Unfortunately, the disadvantage of such a system is that the power of available semiconductor lasers is insufficient to meet the concentration and range requirements. In general the laser power would have to be improved by approximately twelve orders of magnitude to meet the desired specifications (Figure 18). Of interest, however is that at the 10 meter range an improvement of only five orders of magnitude will enable methane concentrations of 1.5% to be measured with the desired accuracy and resolution (Figure 19).

In summary, although the use of semiconductor lasers offer the promise of a portable system the laser power is currently not sufficient for our purposes. The technology is however, being driven by a wide variety of factors and in the near future more powerful semiconductor lasers will be developed.

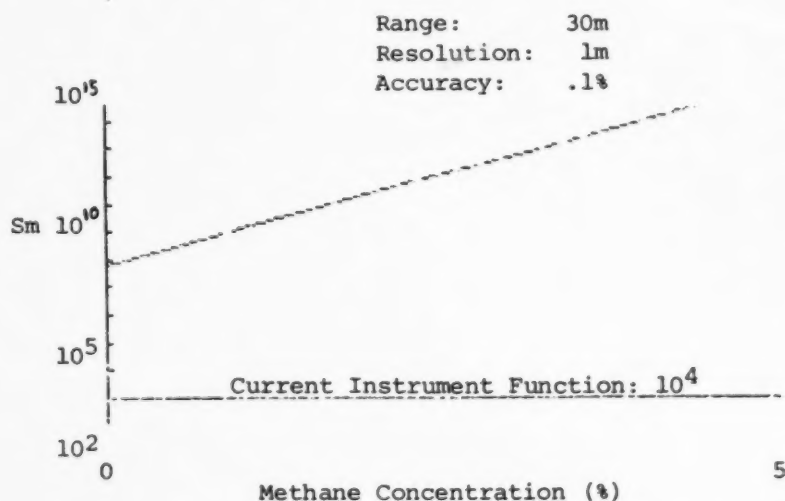


Figure 18: Plot of Measurement Function
versus Concentration at 30 meters

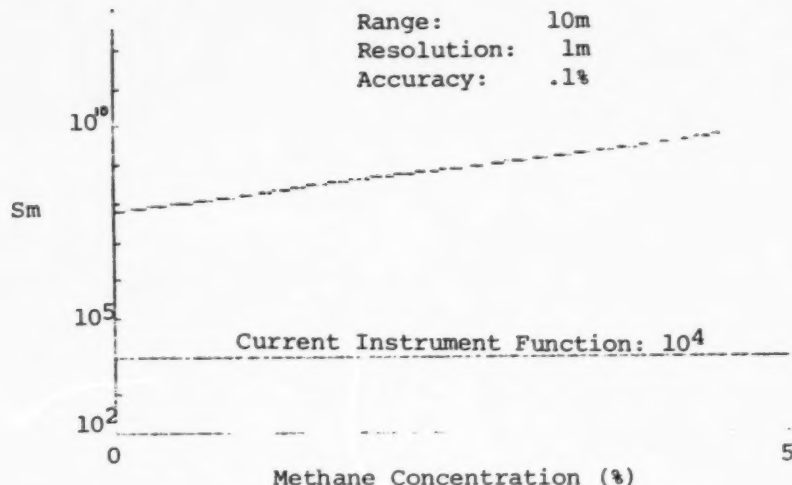


Figure 19: Plot of Measurement Function
versus Concentration at 10 meters

7.4.2 Er:YAG Laser

A system utilizing a Er:YAG tunable, pulsed laser in an off-axis configuration offers the best choice for a semi-portable underground methane analyser. Although not a truly portable system, the technique has been demonstrated to be capable of almost meeting the desired range and concentration specifications (Section 6.3).

Figure 20 is a plot of the measurement function versus concentration based upon our understanding of the system. It shows that the system is currently capable of measuring methane concentrations of up to 4% at the 10 meter range with an accuracy of 0.3% and with a resolution of 0.3 meters. Figure 21 is the same plot at 30 meters with a resolution of 1 meter and an accuracy of 0.1%. It illustrates that the system would currently only be able to measure methane concentrations up to 1% and that an improvement of five orders of magnitude would be required to meet the desired specifications at 30 meters.

The two major disadvantages of the above system are that it is currently only capable of a fixed range resolved measurement and the procedure to tune the laser is time consuming and requires a skilled operator. Although the use of AOTF would simplify the tuning procedure it appears that development in this area is minimal. An automated source or detector scanning arrangement will have to be implemented to provide for variable range resolution however, this will result in an increased analyser size.

In summary, although the aforementioned system cannot be considered truly portable it does offer the benefit of being able to measure methane concentrations in the range of interest. Additional development of this technology, i.e. implementation of a scanning mechanism, should result in a semi-portable system for underground methane measurements.

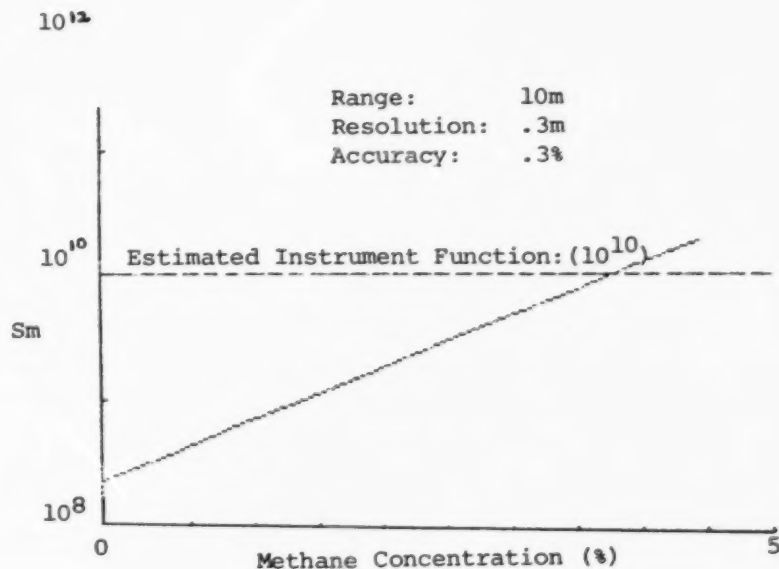


Figure 20: Plot of Measurement Function versus Concentration at 10 meters

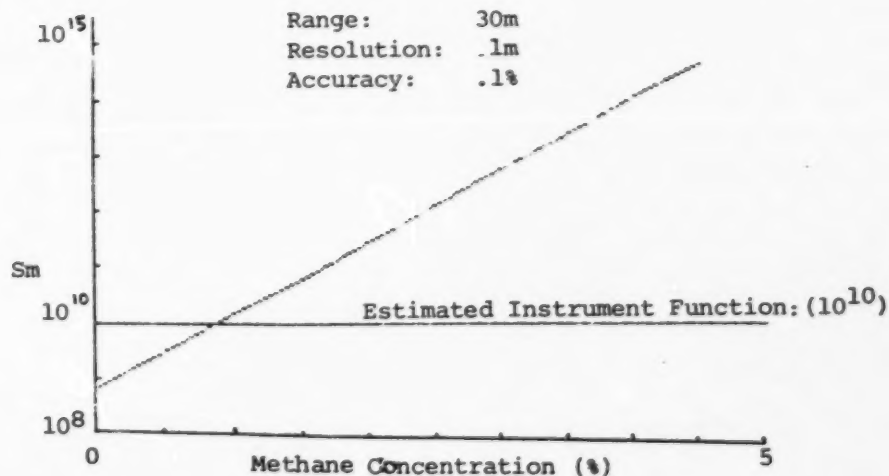


Figure 21: Plot of Measurement Function versus Concentration at 30 meters

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Program for calculating the measurement function for the Raman scattering technique.

```

1000 1 ***** CALCULATION START
1001 1
1002 FOR Q=1 TO 3
1003 R5=0
1004 FOR P=M1 TO M2 STEP M3
1005 R5=R5+1
1006 C1,Q,R5)=32*(C/S(Q))^2*R-2*(C*
1007 G*D*(Q)*PI)
1008 NEXT R
1009 NEXT Q
1010 1
1011 1 ***** CALCULATION END
1012 1
1013 1 ***** PLOTTING START
1014 1
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Program for calculating the measurement function for the differential absorption technique.

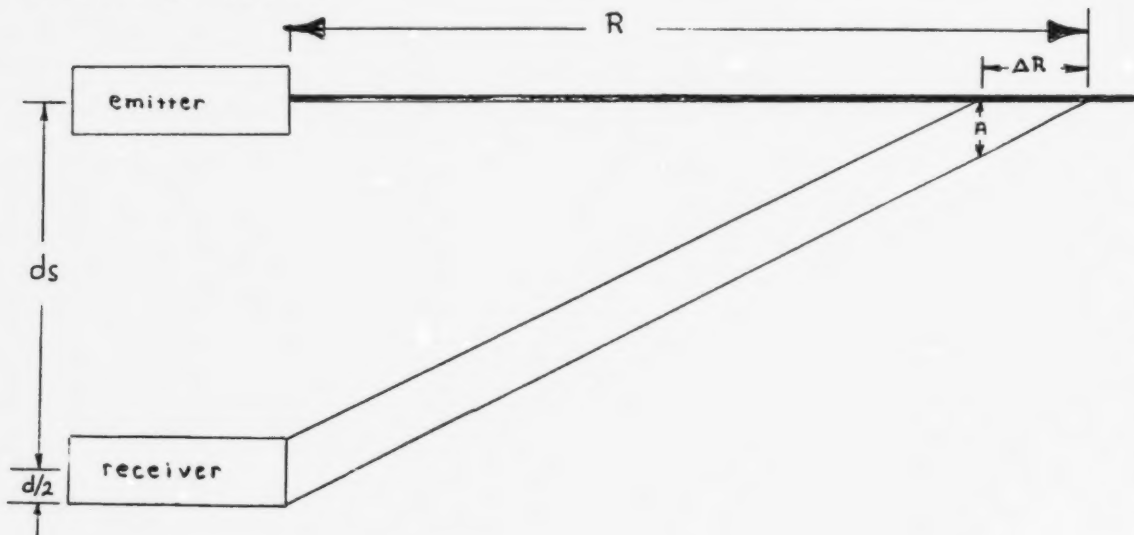
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APPENDIX III

Derivation of the relationship between the receiver/emitter separation and the receiver aperture diameter.

The optical arrangement of an off-axis system with spatial resolution capabilities can be approximated as shown in the following figure.



The relationship can thus be written as:

$$\frac{R}{ds + d/2} = \frac{\Delta R}{A}$$

Where ΔR is relatively small compared to R , the term (A) can be approximated by the diameter of the aperture (d) . The relationship can therefore be expressed as:

$$\frac{\Delta R}{R} = \frac{d}{ds + d/2}$$